THE DETERMINATION OF SODIUM, POTASSIUM AND TITANIUM IN CLAY BY FLAME SPECTROPHOTOMETRY

A THESIS

Presented to

the Faculty of the Graduate Division

Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

By

Donald Paul Schlueter

September 1955

Original Page Numbering Retained.

5P
12T

THE DETERMINATION OF SODIUM, POTASSIUM AND TITANIUM IN CLAY BY FLAME SPECTROPHOTOMETRY

Approved:

Date Approved by Chairman: August 18, 1955

ACKNOWLEDGEMENT

I wish to extend my sincere thanks and appreciation to Dr. W. C. Whitley for suggesting the problem and for his invaluable suggestions during the course of the research. I also wish to express my thanks to my wife, Doris Schlueter, for her patience and constant encouragement.

TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

THE DETERMINATION OF SODIUM, POTASSIUM AND TITANIUM IN CLAY BY FLAME SPECTROPHOTOMETRY

CHAPTER I

INTRODUCTION

The complete analysis of clays has been a lengthy and tedious operation for many years. The procedures used involved gravimetric, volumetric and to a limited extent instrumental analysis.[1,2,3] Since the majority of the constituents in clays, excepting silica and aluminum, are present in concentrations of one percent or less, considerable experience is necessary to obtain accurate and reproduceable results.

The J. Lawrence Smith method[4,5] is the most widely used procedure for the determination of the alkalies in silicate materials. This method involves the separation of the alkalies as chlorides, removal of calcium as the carbonate and determination of sodium and potassium as the combined chlorides. The potassium is then determined as the chloroplatinate and the

---

1. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I., Applied Inorganic Analysis Second Ed., John Wiley & Sons, Inc., (1953) pp. 793-956
2. Shapiro, L and Brannock, W. W., Geological Survey Circular 165, (1952)
3. Shell, H. R., Bureau of Mines Report of Investigations, 4420, (1949)
4. Scott, W. W., Standard Methods of Chemical Analysis, Fifth Ed., Vol. I. D. Van Nostrand Co., Inc., (1939) p. 882
5. Shell, op.cit. pp. 26, 27

value of sodium obtained by difference. This procedure involves numerous separations, and since the sodium is determined by difference any contamination will seriously affect the results. The introduction of some instrumental method of analysis would not only decrease the time involved but also improve the accuracy obtainable by a less experienced analyst.

The flame photometer was selected for the instrumental analysis because of its inherent sensitivity for the alkalies and its ease of operation.

In flame photometry, solutions are atomized into the flame of an oxyhydrogen burner, and the concentrations of the relatively easily excited metals are determined by measuring the intensity of a part of their characteristic spectral emissions and comparing the emissions with those of solutions of known concentrations.

The emission intensities which are measured in flame photometry result from atomic spectra. The electrons of an atom may be considered to be arranged around the nucleus in groups or "shells" that increase by one electron as the atomic number of the element increases by one, up to a point where a shell is filled, whereupon another shell starts. At the higher atomic numbers, incomplete shells may be formed which remain so even after another shell has been started.

The outermost electrons are those most likely to absorb additional energy momentarily. This added energy may be supplied by a high temperature flame or arc.

When such energy has been supplied, an electron in its normal orbit is moved some added distance from the nucleus. The energy absorbed, or the distance moved is not continuously variable but consists of definite steps or levels. An electron so removed from the nucleus may give up some energy and drop to a lower level, and eventually reach the unexcited or ground state after a series of steps, or it may give up all of the energy in one step and reach the ground state. As energy is released it is emitted in the form of light. The frequency of the light emitted is proportional to the change in energy experienced by the electron in moving from an upper state to a lower one.

Since the energy released consists of definite amounts, which are related to the attractive forces between electron and nucleus, one type of atom has a limited number of possible modes in which energy may be released. There are, consequently, only certain frequencies of light which can be produced by a certain kind of atom. A measurement of the frequencies, or wavelengths, of light emitted by an atom therefore constitutes a possible method of identification of that atom, and the spectrum is termed the atomic or line spectrum. The greater the energy in the excited source, the higher the energy of the excited electron, therefore more lines may appear. However, the wave lengths of the existing lines will not be changed. The intensity of a spectral line depends mainly on the probability of the required energy "jump" or transition taking place.

In 1929 Lundegardh[6] described a procedure in which the intensities of spectral emissions obtained when solutions were atomized into a flame were determined by measuring the density of lines on photographic plates as in spectrographic techniques. Flame photometry differs from Lundegardh's procedure in that spectral emissions are measured directly with a photometer.

In 1946 Barry, Chappell, and Barnes[7] described a flame photometer with a dual optical system designed for use with lithium as an internal Standard, as well as for direct intensity determination. In procedures using an internal standard the intensity of the emission of the unknown element is compared simultaneously with the emission of the internal standard, which has been added to the sample and standard solution in like amounts. This internal standard technique reduces the disturbing effects of variation in flame character caused by changes in gas and oxygen pressures, the presence of foreign salts, and differences in viscosity of the solutions. This method has the disadvantage that unsuspected errors may arise from its use. If the test sample should actually contain some of the internal reference element, a corresponding error would result. More serious is the fact that the emissions of the

---

6. Lundegardh, H. Die Quantitative Spectroanalyse der Elemente, Pt, Jena, Gustav Fisher (1929)

7. Barry, J. W., Chappell, D. G. and Barnes, R. B., Ind. & Eng. Chem., Anal. Ed., 18, 19-24, (1946)

internal standard element and the element being measured are usually influenced differently by variations in flame temperature and often by the presence of other components in the sample as well.

In 1948, National Technical Laboratories began producing a flame attachment for their model DU quartz spectrophotometer.[8] This instrument overcame some of the short comings of previously described instruments with respect to convenience and speed of operation, accuracy of measurement and freedom from spectral interference in multi-component solutions.

The most important advantage of this instrument is the fact that it contains a quartz monochromator which provides a continuous selection of wavelengths with resolving power sufficient to separate completely most of the easily excited emission lines, and freedom from scattered radiation sufficient to minimize interferences. This type of instrument is not readily adaptable to the internal standard method. However, it has been pointed out that there are several serious disadvantages to the internal standard method. The Beckman DU with flame attachment was used in this research.

The preferred way of standardizing a flame photometer of this type is to prepare standard solutions which approximate the test samples in composition and to standardize the instrument with the element that is being determined.

---

8. Gilbert, P. T., Hawes, R. C., and Beckman, A. O., Anal. Chem. 22, 772, (1950)

Interferences often are the most troublesome aspect of flame photometry, and are the most hazardous to analytical accuracy because they may exist unsuspected. Since a major portion of this research involved the study of interferences, they will be discussed here in some detail.

Variations of the apparent or actual emission of radiant energy by excited atoms or molecules or radicals containing atoms of the species sought may arise in the following ways: 1. Such mechanisms as quenching, sensitization, reabsorption (reversal) and variations in combustion processes, resulting in altered flame temperature, may cause alteration of the energy, in an emitted line or band by other substances in the flame. Quenching and sensitization involved photochemical effects. In the discussion concerning the excitation of an atom, which results in the radiation of energy at a wavelength characteristic of that element, it was assumed that the excited particle is not deprived of its energy by collision with another particle, either of the same or of a different chemical nature. This would pre-suppose a negligible pressure for the burner gases. However, at ordinary pressures one molecule collides with another, once in approximately 10^{-10} seconds, so that there should be many collisions during the life of an excited molecule. As a result, removal of energy does occur as the gas pressure becomes appreciable. This can be shown by the fact that inert gases are able to diminish or quench fluorescence: for example, hydrogen at a pressure of 0.2 mm of mercury is

able to reduce the resonance radiation of mercury vapor to one-half of its original value.[9] Although other gases are not so effective, they still have a marked influence. Deactivation does not always occur at every collision. This brings out the important fact that transfer of electronic energy in collisions is highly specific, and depends both on the nature of the inert gas and the excited particle. For example, hydrogen is more effective than nitrogen in quenching the resonance radiation of mercury vapor at 18°C, but the reverse is the case for sodium vapor at 200°C.

If the vapor of thallium or an alkali metal is added to mercury vapor and exposed to the exciting radiation of 2537 A wavelength, the resonance fluorescence radiation emitted contains lines of the spectrum of the added substance; the strongest lines are generally those of frequency nearest to that of the original light. The interpretation of this result, e.g., with thallium, is that the mercury vapor absorbs the 2537 A radiation and the atoms become excited; in collision with atoms of thallium, however, a proportion of the excitation energy is transferred to the latter, which are raised to higher electronic levels, i. e., mainly 2^2S and 3^2D.[10] The remainder of the energy is converted into kinetic energy. As the excited

---

9. Glasstone, S., Textbook of Physical Chemistry, D. Van Nostrand Co., Inc., (1940) p. 1132.

10. Glasstone, op.cit., p. 1133

thallium atoms return to lower energy states the appropriate fluorescence radiation of thallium is emitted. This type of behavior is known as sensitized fluorescence; because of the presence of the mercury, the thallium is rendered fluorescent by radiations which would normally not be absorbed and would consequently have no effect.

Reabsorption or reversal is a characteristic of atomic emission spectra. Since an excited atom may give off energy as light and return to the ground state, it follows, conversely, that an atom in the ground state may absorb energy in the form of light. If there are relatively few atoms of a certain kind in a flame, and correspondingly few atoms of that type in the cold vapor surrounding the discharge, then the probability is high that any light emitted by such an atom will pass out of the flame and reach the slit of the spectrophotometer without being absorbed by a similar atom. As a consequence, the light passing into the spectrophotometer will be proportional to the amount of light emitted.

As the concentration of those atoms in the flame increases, and the concentration of atoms in the cold vapor correspondingly increases, then the probability of absorption becomes greater. Eventually some point is reached where an increase in the number of atoms, and the light emitted by them in the flame, no longer changes the intensity of a particular wavelength of light reaching the spectrophotometer. As the concentration is increased still more, and the number of atoms

in the vapor becomes very high, then eventually a point will be reached where the light emitted is nearly all absorbed before it reaches the slit of the spectrophotometer. The line is then said to be reversed. For this reason it is adviseable, especially where the concentration of interfering ions is high, to operate at high sample dilution.

2. Energy at other wavelengths than those intended to be measured may reach the photodetector. The monochromator must be capable of excluding emission at wavelengths adjacent to or remote from the selected band by substances uncontrolled in the comparison standards. The Beckman model DU satisfies this condition.

3. Direct interference by (nonbackground) radiation can occur when a desired line falls within a molecular emission band. When emission bands actually overlap, interference cannot be obviated by increased resolution. An example would be a sample containing barium and lanthanum. The barium emission at 515 to 550 mμ would be convenient to use were it not for the lanthanum (oxide) bands which interfere. Conversely, unresolved barium bands interfere with the lathanum band at 563 mμ. Here the solution lies in selection of other spectral regions where mutual interference does not occur. The lanthanum peak at 798 mμ and the barium emission at 830 or 873 mμ are much less subject to mutual interference and are more sensitive than the green bands.

4. Intense adjacent line emission can also cause direct interference. Sometimes an extremely brilliant atomic emission may

interfere with the measurement of a neighboring line, either through Doppler broadening or because scattered radiation tends to be concentrated near the line image. An example is found in the determination of boron in borax. The boron band at 548 mμ cannot be used because of the overwhelming brilliance of the sodium D doublet from solutions sufficiently concentrated to permit determining boron to one percent of its amount. However the boron bands at 495 and 521 mμ can be used without interference from the sodium.[11]

5. A general increase of flame background at all wavelengths may occur and is common with materials containing sodium and potassium. It extends over most of the spectrum, but is not due to scattered light. Dean[12] suggests that this interference may be due to chemiluminescence which results in higher temperatures in the outer mantle of the burner. In practice such background corrections can be either measured or obviated by use of a blank containing the proper amount of interfering metal but none of the metal being determined.

6. Spray rate alteration by uncontrolled constituents or by conditions which affect the hydrodynamics of the atomizer is a common cause of interference. Both the viscosity and the surface tension of the solution are of first importance in determining the rate of introduction of the sample into the flame of

---

11. Gilbert, op.cit. p. 777

12. Dean, J. A., and Burger, J. C. Jr., Anal. Chem., pp. 27, 1055, (1955)

a given burner. This difficulty is overcome by employing standards which are similar in composition to the samples.

After reviewing the various types of interference encountered in flame photometric analysis, the necessity for a complete study of interferences in developing a method of analysis of a particular constituent is obvious.

The original objective of this research was to develop routine methods of analysis, employing the flame photometer, for as many constituents which are normally found in clays as possible. Due to the vast scope of this project it was necessary to limit this particular phase of the work to the analysis of sodium, potassium and titanium. An outline of a proposed scheme of analysis for clays, using the flame photometer is given in the summary. (Chapter VI)

CHAPTER II

SOLUTION OF CLAY SAMPLES

Two methods for the solution of silicious materials are in general use, one involving alkali fusion the other acid digestion with hydrofluoric acid in combination with one or more strong acids.[13,14,15,16] The choice of methods to be used in this research was limited to the acid digestion, since it was desired to analyze as many constituents of the clay as possible with the flame photometer using a single sample. The addition of alkali in the fusion process would not only prevent the analysis of the alkali metals in the sample but would also introduce serious interferences in the flame photometric determination of constituents other than the alkali metals.[17,18,19,20]

---

13. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I. Applied Inorganic Analysis, John Wiley & Sons, Inc., (1935) pp. 836, 850.

14. Shapiro, L., and Brannock, W. W., Geological Survey Circular, 165 (1952) p. 5.

15. Corey, R. B. and Jackson, M. D., Anal. Chem. 25, 624,(1953)

16. Brannock, W. W. and Berthold, S. M., Geological Survey Bulletin 992, (1949) p. 3.

17. Eggertsen, F. T., Garrard, W. and Lykken, L., American Society for Testing Materials, Special Technical Publication, No. 116, p. 58. (1951)

18. Porter, P and Wyld, G., Anal Chem., 27, 733, (1955).

19. Kinsvark, O. N., Wittwer, S. H. and Sell, H. M., Anal Chem. 25, 320 (1953)

20. Knight, S. B., Mathis, W. C. and Graham, J. R., Anal Chem. 23, 1704, (1951)

The most common acid mixtures used consist of H_2SO_4-HF, H_2SO_4-$HClO_4$-HF and $HClO_4$-HF. The disadvantage of the H_2SO_4-HF mixture lies in the fact that fluorine is incompletely expelled. The formation of sulfates rather than the more soluble perchlorates is also somewhat undesirable. The elimination of all fluorine can be made certain if, after the solution has been heated to fumes of sulfuric acid, it is cooled, the inside of the dish is washed down with a little water, and the solution is again heated to fumes after the addition of a moderate excess of pure powdered silica.[21]

In some cases, especially when alkaline earths are present, decomposition by use of hydrofluoric and perchloric acids possess an advantage in that the attack yields soluble perchlorates which cause no difficulties in a succeeding operations. The perchloric acid also serves to destroy any organic material which may be present in the sample.[22] However, as a rule, the expulsion of hydrofluoric acid is more difficult when perchloric acid is used and the heating should be carried on until a dry residue is obtained.

When the H_2SO_4-HF mixture is used to digest the sample nitric acid can be used to destroy the organic material which may be present.

---

21. Hillebrand, W. F., Lundell, G. E., Bright, M. S. and Hoffman, J. I. Applied Inorganic Analysis, John Wiley & Sons Inc., (1953) p. 850.

22. Corey, op.cit., p. 625.

Another possible method involves the decomposition of the sample with hydrochloric or perchloric acid followed by dehydration of the silicic acid formed. The SiO_2 may be filtered off and again extracted with acid to remove soluble salts. This method is not very reliable since it is difficult to entirely remove all of the salts from the SiO_2 formed, and since dehydrated silica is slightly soluble in solutions of alkali chlorides, which are always present in the samples, an inherent error is thus introduced.[23]

Mosher[24] used the HCl digestion method for the preparation of samples of Brucite and Magnesite prior to the flame photometric determination of calcium. Due to the composition of the clays to be analyzed this method did not appear suitable.

The majority of clay samples encountered in routine analyses contain varying amounts of organic material. For complete solution of sample this must be destroyed either by ignition of the dry sample or chemical oxidation. Removal of the organic material by ignition was investigated but was found unsatisfactory because of possible volatilization of the alkali metal oxides and the formation of an insoluble form of aluminum oxide. The chemical method of oxidation employing concentrated nitric acid proved to be completely satisfactory for destruction of organic material in all the clays investigated.

---

23. Scott, W. W., Standard Methods of Chemical Analyses, Vol. I, Fifth Ed., D. Van Nostrand Co., Inc. (1939) pp. 800,802.

24. Mosher, R. E., Bird, E. J., and Boyle, A. J., Anal Chem. 22, (1950)

The perchloric-sulfuric acid mixture appeared desirable since the organic material would be destroyed by the perchloric acid. This digestion method was applied to a number of clay samples but always resulted in considerable insoluble residue remaining on the addition of water. Low results for potassium were obtained employing this digestion method. Considerably more time was necessary for the H_2SO_4-$HClO_4$-HF digestion than the H_2SO_4-HF digestion to obtain complete solution.

The following procedure was adopted for the solution of all clay samples investigated. One-half gram samples of clay were placed in fifty milliliter flat bottom platinum dishes and treated with 10 ml of one to one sulfuric acid and 15-20 ml of 47 percent hydrofluoric acid. The samples were evaporated to fumes of sulfur trioxide and concentrated nitric acid then added dropwise to destroy any organic material which may have been present. Complete destruction was evident when the solutions became clear light yellow or colorless. The solutions were then evaporated to near dryness using overhead heat from an infra-red lamp to reduce spattering and save time. Several evaporations may be necessary for complete solution. About 25 ml of water and 3 ml of 1:1 sulfuric acid were added and the solutions heated until all the salts were completely dissolved. This usually required 30-45 minutes. Finally, the samples were transferred to 100 ml volumetric flasks, cooled and diluted to volume. Aliquot portions of these sample solutions were then taken for the subsequent analyses.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

The instrument used for the analytical work in this research was a Beckman Model DU spectrophotometer equipped with a model 9200 flame attachment. A Model 4020 hydrogen-oxygen burner was employed as the exciting source. To increase the sensitivity of the instrument in the spectral region below 600 mμ a Beckman Model 4300 photomultiplier was added. This attachment increases the sensitivity of the spectrophotometer at least one-hundred fold in the range 200-600 mμ. An overall view of the spectrophotometer, gas pressure controls, and burner assembly is given in Figure 1.

The determination of sodium, potassium and titanium require different instrument settings and sample preparation. These conditions will be discussed in detail in Chapters IV and V. However, a general instrumental procedure will be given in this section.

Instrumental Procedure. The Beckman Model DU spectrophotometer employs conventional electronic circuits and therefore, requires a "warm-up" period of about forty-five minutes for maximum stability. The selector switch is set in the "check" position during this period and the shutter switch in the "off" position. The proper phototube must be selected, i.e., the red tube above 600 mμ-lever in - , and the photomultiplier tube - lever out - below 600 mμ. If the photomultiplier tube is used,

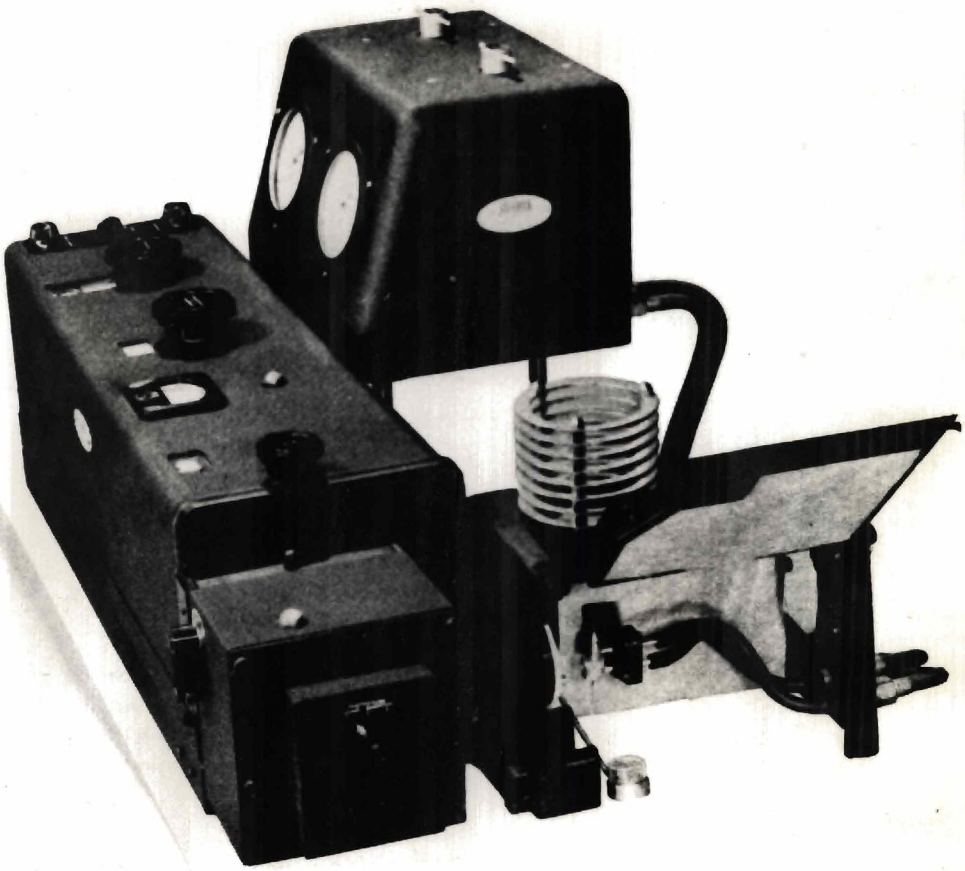


Figure I. The Beckman Model DU Spectrophotometer With a Model No. 9200 Flame Attachment

its power supply is also turned on about 45 minutes before use. Next the proper load resistor is selected. The 2000 megohm resistor (position 2 on the resistor selector box) is used for flame photometry below 600 mμ and the 10,000 megohm resistor (position 3) is used for flame photometry above 600 mμ. The proper wavelength is selected depending on the element to be determined. The sensitivity control setting will also depend on the element being determined, for sodium and potassium it is at the midpoint position, for titanium at the full counter-clockwise position. After a suitable "warm-up" period the selector switch is set at the 0.1 position and the dark current adjusted to zero the galvanometer. The spectrophotometer is ready to measure the emission of elements excited by the burner.

Flame attachment. An oxy-hydrogen burner was employed as the exciting source in this research. Reducing valves on the cylinders were set at 40 pounds per square inch for oxygen and 10 pounds per square inch for hydrogen. The regulators on the instrument panel were set at 11 psi for oxygen and 5 psi for hydrogen. These pressure settings will be different for different burners. In lighting the burner the oxygen and hydrogen control valves are opened slightly and then set to the required pressure after the burner has been ignited.

Analytical Procedure. The concentration of a given element is determined by comparing the intensity of a part of its character-spectral emission with the emissions of solutions of known

concentrations in a region which encompasses that of the samples, must be prepared. They are referred to as standard solutions and are prepared from very pure salts of the elements to be determined. For example, in the determination of sodium, standard solutions of 5, 10, 25, 50, 75 and 100 ppm were prepared from C.P sodium chloride, previously dried for two hours at 110° C. Portions of each of these standard solutions and of the sample solutions were transferred to five ml beakers. A beaker was inserted in the beaker support of the instrument. The dark current was adjusted to zero the galvanometer and the shutter was then opened. The beaker was raised so that the solution was aspirated into the flame. The percent transmission dial was rotated to again zero the galvanometer. This procedure was repeated three times and the average of the three intensity readings recorded. After the emission values were obtained for all the standards, the emission intensities of the samples were measured. When these values were obtained for the samples they were rerun, bracketing each sample with a standard of higher concentration and one of lower concentration. The concentration of the sodium in the sample was then obtained by interpolation. A correction for background was made by measuring the emission of the solvent and subtracting this value from the emission of the standards. A blank correction for the samples was made by measuring the emission of a blank carried through all the steps used in preparing the samples and subtracting this from the emission intensities of the samples.

Interference Measurements. The following procedure was used to study the interference effect of one element upon the flame photometric determination of another element. To study these interferences solutions were prepared holding the concentration of the element, upon which the effect was being measured, constant and varying the concentration of the interferring element. Table 1 lists the salts which were used in the study of interference effects on the determination of sodium, potassium and titanium in flame photometry.

Table 1. Salts Used for Interference Studies in the Flame Photometric Determination of Sodium, Potassium and Titanium

Interferring Element	Salt Used	Solvent
Aluminum	$AlCl_3$ C.P.	10% HCl
Calcium	$CaCO_3$ C.P.	10% HCl
Iron	Iron Wire B.S.	$HCl-HNO_3-H_2O$
Magnesium	$MgCl_2 \cdot 6H_2O$ C.P	10% HCl
Potassium	KCl C.P.	H_2O
Sodium	NaCl C.P.	H_2O
Titanium	TiO_2 B. S.	$H_2SO_4-(NH_4)_2SO_4-H_2O$
Vanadium	NH_4VO_3 C.P.	10% HCl
Zirconium	$ZrOCl_2 \cdot 8H_2O$ C.P.	5% HCl

Standard solutions of the element under investigation were prepared at the concentration which was to be held constant and also one of slightly higher and one of slightly lower

concentration. The latter two solutions were necessary to make the numerical corrections in the concentration of the element being held constant. The emission intensities of these solutions were measured followed by measurements of the intensities of the solutions containing various concentrations of the interferring elements. The difference in emission between the latter solutions and that of the standard solution containing no interferring elements was used to calculate the apparent concentration of the element being determined. Details of these interference studies are given in Chapters IV and V.

CHAPTER IV

THE DETERMINATION OF SODIUM AND POTASSIUM IN CLAY

The widespread use of the flame spectrophotometric analysis of the alkali metals is attested by the voluminous publication in this field in recent years. Several papers have been published on the determination of the alkalies in portland cement and refractory materials.[25,26,27,28,29] Knight, et.al., [30] described a method for the determination of lithium, sodium and potassium in limestones and various glasses. A method for determining all the alkali metals in glasses and ores is described by Williams.[31] The analysis of sodium and potassium in silicious materials was demonstrated by Brannock and Berthold [32] and later by Corey and Jackson.[33] However, in all of the instances mentioned above an internal standard type of flame

---

25. Diamond, J. J., and Dean, L., American Society for Testing Materials, Special Technical Publication No. 116, 28,(1951)
26. Ibid., Gilliland, J. L., p. 33.
27. Ibid., McCoy, W. J., and Christiansen, G. G., p. 44
28. Ford, C. L., Anal. Chem., 26, 1578, (1954)
29. Diamond, J. J., Bean, L., Anal. Chem., 25, 1825, (1953)
30. Knight, S. B., Mathis, W. C., and Graham, J. R., Anal. Chem., 23, 1704, (1951)
31. Williams, J. P., J. Amer. Cer. Soc., 37, 306, (1954)
32. Brannock, W. W. and Berthold, S., Geological Survey Bulletin, 992, 3, (1949)
33. Corey, B., op.cit. p. 625

photometer was used. In this investigation of clay analysis a Beckman Model DU spectrophotometer was used and therefore, the internal standard method could not be used. This necessitated a complete study of interferences and the development of a method which would eliminate or correct for these interferences.

Standard curves of emission vs. concentration were prepared for sodium and potassium to determine whether a linear relationship existed. Standard solutions of sodium and potassium in concentrations of 5 to 100 ppm were prepared by diluting the required amount of stock solutions to 100 mls. The

Table 2. Instrument Settings for the Determination of Sodium

Selector switch	0.1
Sensitivity	Midpoint
Slit width	0.01
Wave length	588 mμ
Photomultiplier	Number 2
Resistor	2000 megohm
Hydrogen	5 psi
Oxygen	11 psi

Table 3. Instrument Settings for the Determination of Potassium

Selector Switch	0.1
Sensitivity	Midpoint
Slit width	0.045
Wave length	767 mμ
Resistor	10,000 megohm
Hydrogen	5 psi
Oxygen	11 psi

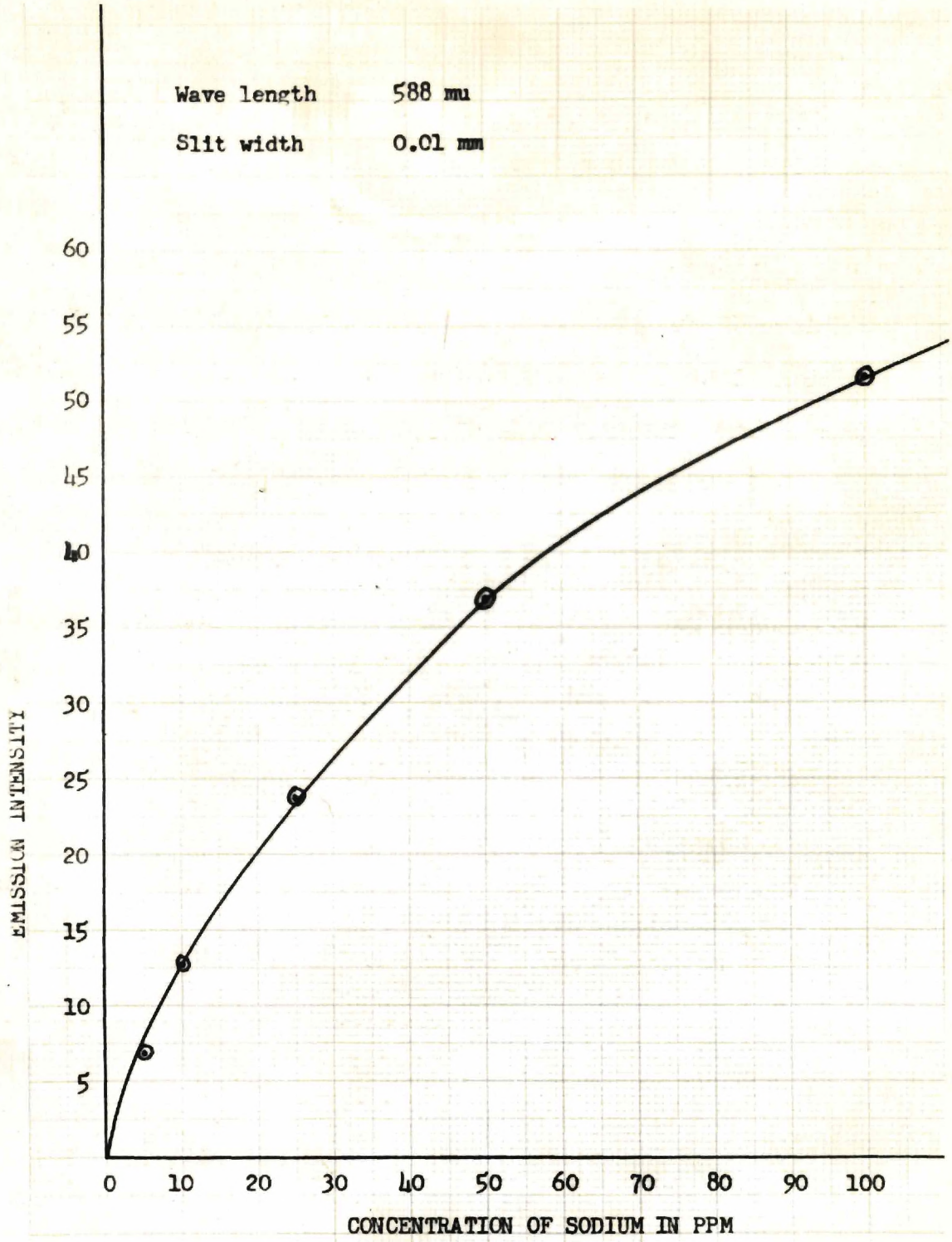


FIGURE 2. STANDARD EMISSION CURVE FOR SODIUM

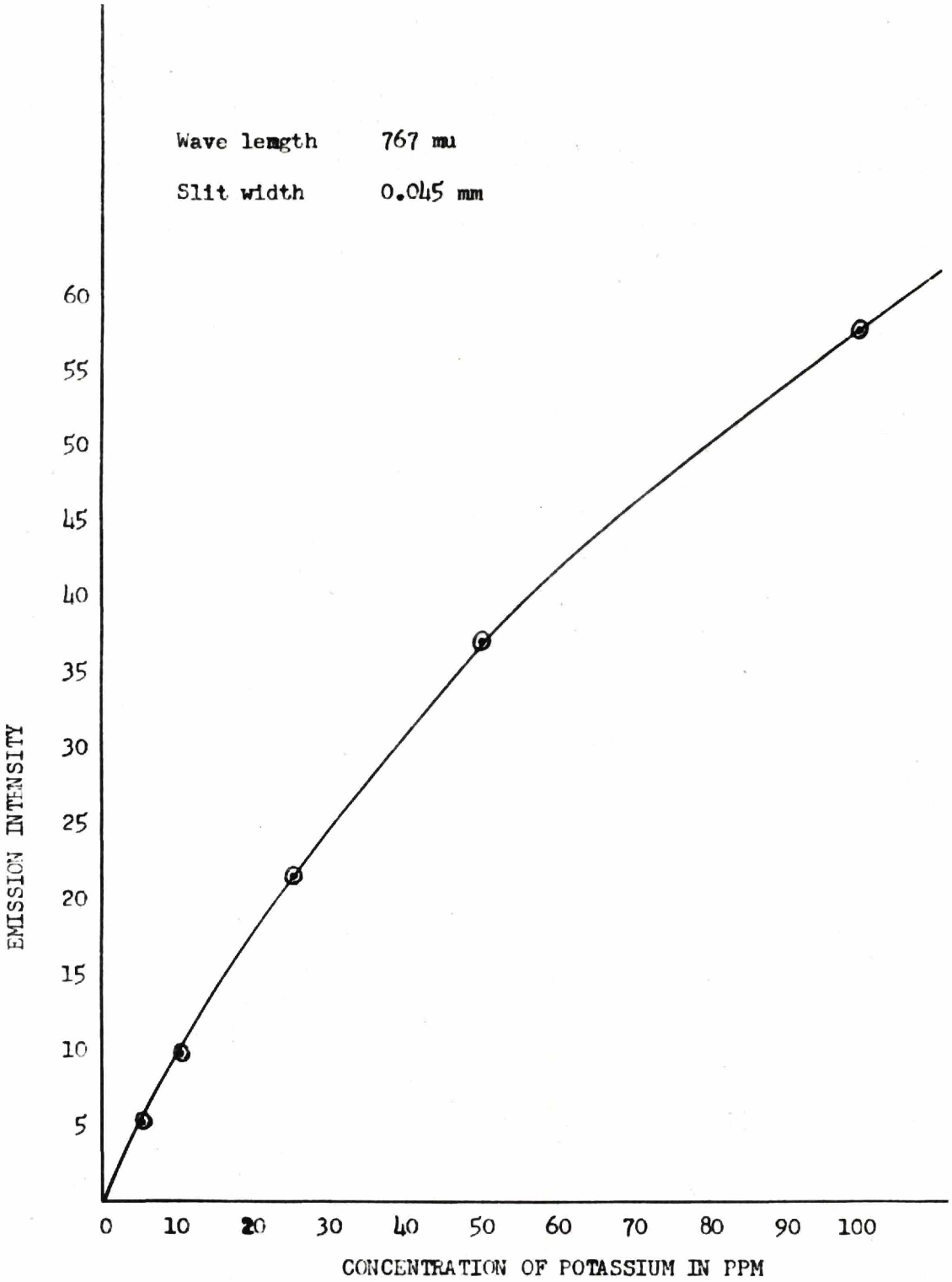


FIGURE 3. STANDARD EMISSION CURVE FOR POTASSIUM

emission values of each standard was measured at the proper instrument settings and these values used to prepare the standard curves. See figures 2 and 3. The instrument settings employed are given in Tables 2 and 3. The plot of emission vs. concentration is not linear for sodium and potassium. The emission values are given in Tables 17 and 18 (appendix). Sodium shows a pronounced upward convexity due to self absorption. This is also true of potassium.

Although the standard curves are not linear, accurate results can be obtained if the unknown sample is bracketed between a standard of slightly higher concentration and one of slightly lower concentration. In any case, the closer the standards are to the sample, the smaller will be the correction for slope and the more reliable the interpolation.

A thorough study of interference effects of other ions, which were present in clays, was undertaken. The results of this study are given in Tables 4 and 5 (appendix). For sodium and potassium the effects of aluminum, iron, titanium and calcium are appreciable. Sodium has a negligible effect on the emission of potassium while potassium enhances the emission of sodium when it is present in concentrations greater than 50 ppm. The interferring ions must be corrected for, or removed from the solution before the sodium and potassium can be determined. The use of standards containing the interferring ions at concentrations approximating those of the sample is a common pratice. However, this procedure would necessitate a rather

complete knowledge of the sample composition. The alternate procedure would involve removal of the interferring ions. Aluminum, iron, titanium and vanadium can be removed by precipitating with ammonium hydroxide while the calcium can be removed by precipitation as the carbonate with ammonium carbonate. The precipitation is carried out in a volumetric flask and after the addition of precipitant the solution is diluted to volume. The error in volume due to the precipitate is negligible.

It was demonstrated that sodium has little effect on the emission of potassium, therefore, it can be determined flame photometrically in the presence of sodium with high accuracy. To determine sodium in the presence of potassium a correction must be made for the enhancement due to potassium. The magnitude of the correction was determined by measuring the emission of a 50 ppm sodium solution to which increasing amounts of potassium were added. The data is given in Table 19 (appendix). It was found that the effect due to potassium was independent of sodium concentration. From the date in Table 19 a correction graph was prepared, Figure 4. This graph can be used to correct the sodium concentration after the concentration of potassium has been determined.

Since the addition of ammonium hydroxide to the sample solution results in the formation of ammonium sulfate,

Table 4. Interference of Various Cations on the Flame Photometric Determination of Sodium

Foreign Cation	Conc. PPM	Sodium Present Conc. PPM	Sodium Found Conc. PPM	Error PPM
Aluminum	550	50	56.7	6.7
	950	50	57	7.0
	1325	50	57	7.0
Calcium	10	50	56	6.0
	50	50	55	5.0
	100	50	53	3.0
Iron (Fe_2O_3)	50	50	54	4.0
	150	50	56	6.0
	250	50	57	7.0
Potassium	10	50	50	0
	25	50	50	0
	50	50	50	0
	100	50	52	2.0
Magnesium	10	50	50	0
	50	50	50	0
	100	50	50.2	.2
Titanium	50	50	51	1.0
	150	50	52	2.0
	250	50	52	2.0

Table 5. Interference of Various Cations on the Flame Photometric Determination of Potassium.

Foreign Cation	Conc. PPM	Potassium Present Conc. PPM	Potassium Found Conc. PPM	Error
Aluminum	530	50	50	0
	1060	50	50	0
	2050	50	49	-1.0
	2650	50	48	-2.0
Calcium	35	50	40.7	-9.3
	71	50	41	-9.0
	107	50	41	-9.0
	214	50	42.2	-7.8
Iron (Fe_2O_3)	50	50	51.7	1.7
	150	50	51.7	1.7
	250	50	51.7	1.7
Magnesium	10	50	50	0
	50	50	50	0
	100	50	50.4	0.4
Sodium	10	50	50	0
	25	50	50	0
	50	50	50	0
	100	50	50.8	0.8
Titanium (TiO_2)	50	50	51.4	1.4
	150	50	50	0
	250	50	49	-1.0

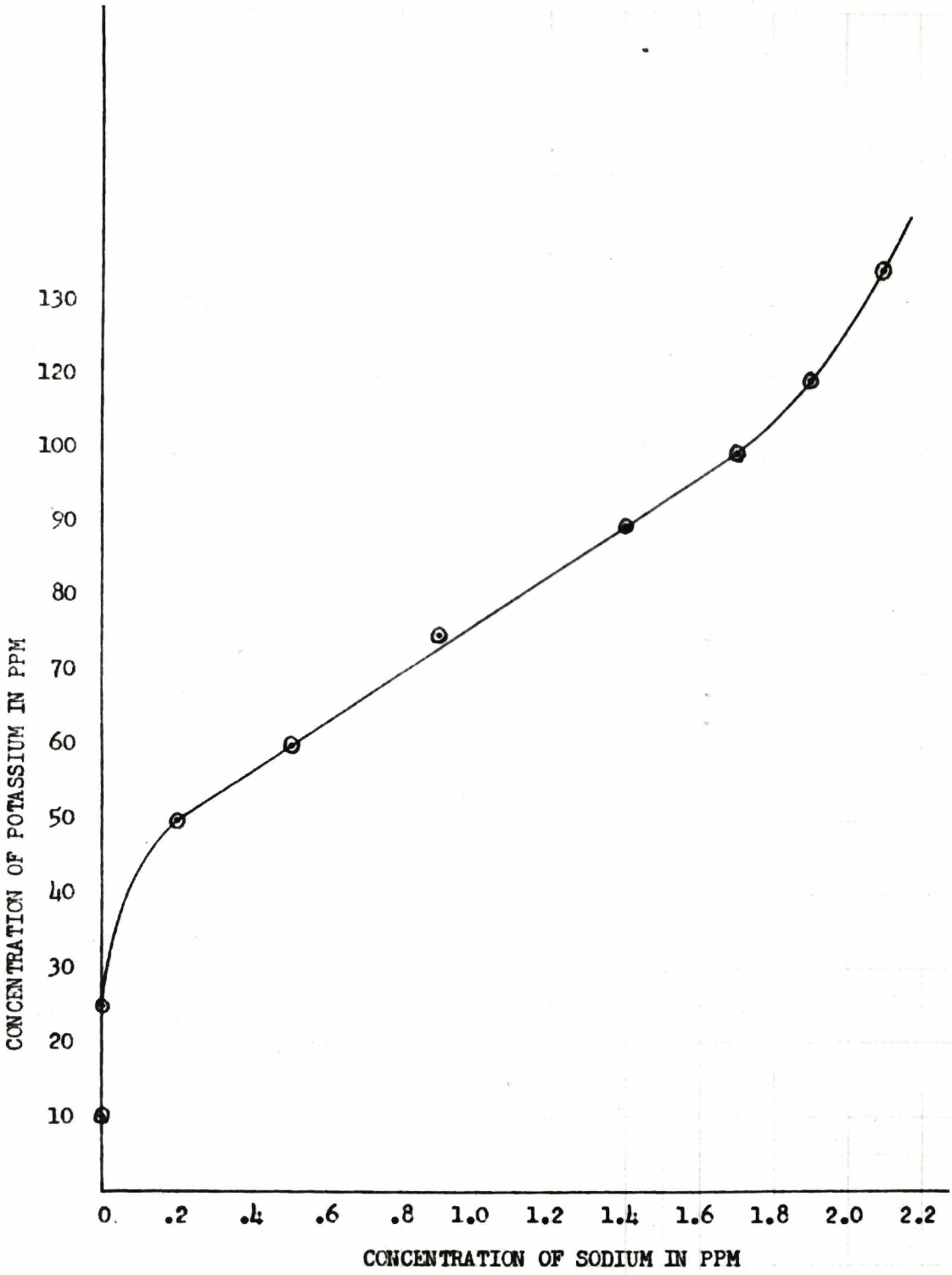


FIGURE 4. CORRECTION FOR SODIUM DUE TO THE PRESENCE OF POTASSIUM

its effect was investigated. It was found that ammonium sulfate had a slight enhancing effect on sodium and potassium emission. This effect was overcome by adding ammonium sulfate to the standard solutions in an amount approximately equal to that which was present in the sample solutions.

The following procedure was used for the analysis of sodium and potassium in clay: a 25 ml aliquot of sample solution -- prepared according to the procedure given in Chapter II -- was transferred to a 50 ml volumetric flask. A small piece of red litmus paper was added to the flask and the solution neutralized with concentrated ammonium hydroxide. One ml of freshly prepared, saturated ammonium carbonate solution was added, the solution was cooled and then diluted to volume. After thorough mixing the solution was centrifuged to settle the precipitate and the supernatant liquid transferred to a 5 ml beaker for determination of sodium and potassium on the flame photometer. The emission of the standard solutions was measured followed by a measurement of sample emission. For more accurate results the sample was run again and the emission of a standard slightly higher in concentration and one of slightly lower concentration was determined. The concentration of the sample was then calculated by interpolation. A sample calculation is given in the appendix. The concentration of potassium was determined first, followed by determination of sodium. With the aid of Figure 4 the proper correction for the sodium concentration was

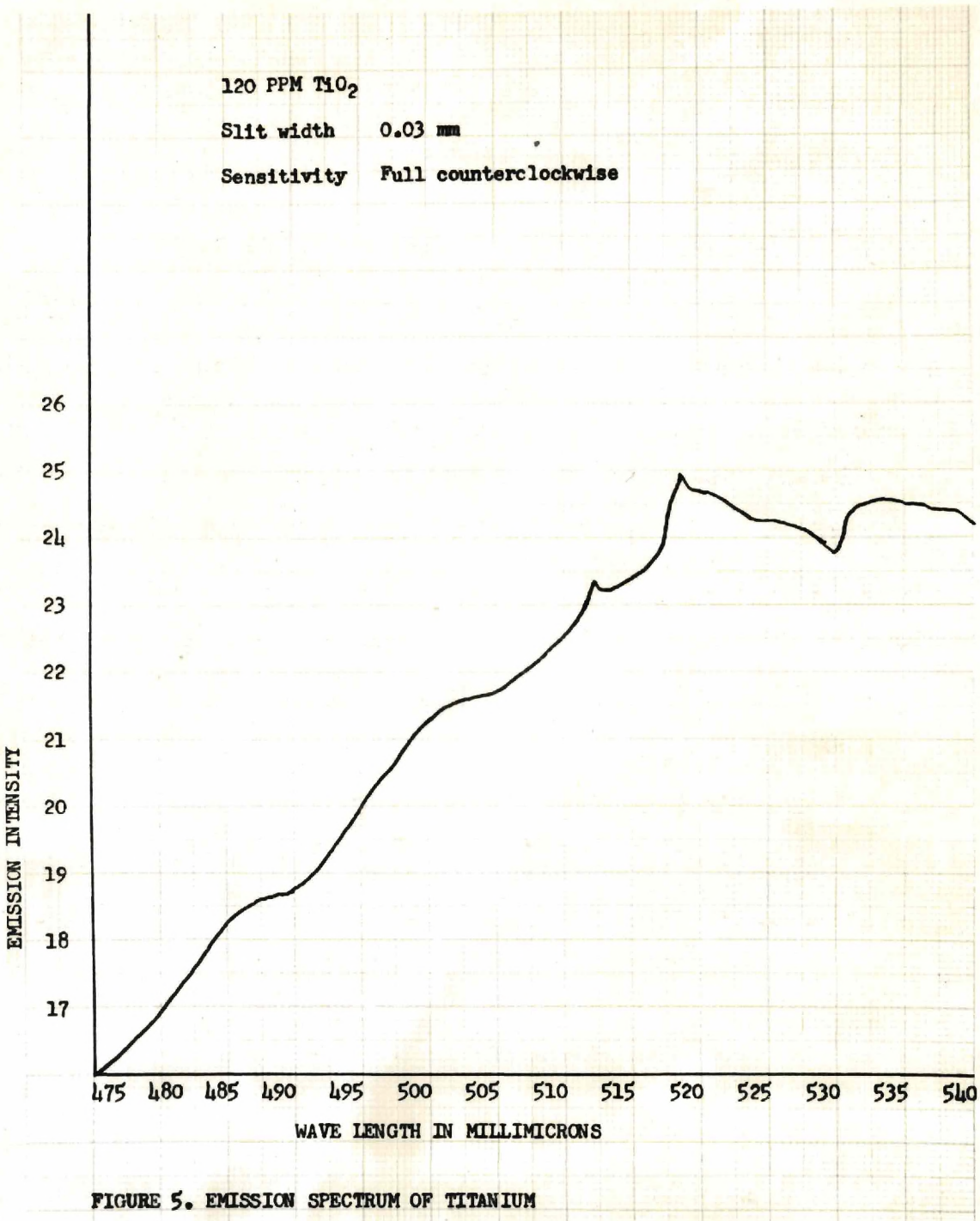


FIGURE 5. EMISSION SPECTRUM OF TITANIUM

then calculated. Table 6 summarizes the results of this method of analysis when applied to a number of clay and synthetic samples. The results obtained for the Bureau of Standard Clay samples are in excellent agreement with those obtained by the more lengthy J. Lawrence Smith method. The clay samples obtained from the American Petroleum Institute gave flame photometric results which differed considerably from the reported results. To further substantiate the procedure used, in light of the results obtained for the four A.P.I. clay samples, two additional samples of siliceous materials obtained from the Bureau of Standards were analyzed. Here again, the results were in close agreement with the reported values, as were the results obtained for the three synthetic samples. This would seem to indicate that the results reported by the A.P.I. were incorrect. Since these samples were processed by a commercial analytical laboratory by the J. Lawrence Smith method this seems quite possible.

The emission intensities for a series of sodium and potassium standards and samples are given in Tables 20 and 21 (appendix). A complete compilation of results obtained for the analysis of sodium and potassium as summarized in Table 6, are given in Table 22 (appendix).

Table 6. Summary of Results of the Determination of Sodium and Potassium by Flame Spectrophotometry.

Sample	No. of Analyses Preformed	%Na_2O Found (Av.)	%Na_2O Reported	%K_2O Found (Av.)	%K_2O Reported
B.S. #97 Clay	12	.06	.06-.08	.54	.54
B.S. #98 Clay	11	.27	.28	3.38	3.17
B. S. #99 soda Feldspar	4	10.71	10.73	.42	.41
B.S. #102 Silica Brick	4	.06	.06	.31	.29
T-1 Clay	5	.04	.40	.17	.43
T-2 Clay	8	.20	.42	.18	.49
T-3 Clay	9	.12	.14	.05	.48
T-5 Clay	6	2.15	1.44	.45	.31
I	2	50ppm	50ppm	50ppm	50ppm
II	2	250ppm	250ppm	250ppm	250ppm
III	2	150ppm	150ppm	151ppm	150ppm

Note: Solutions I, II and III are synthetic samples, whose composition is given in Table 14, Chapter V.
Clay samples T-1, T-2, T-3 and T-5 were obtained from the American Petroleum Institute.

CHAPTER V

DETERMINATION OF TITANIUM

Titanium in clay is determined either gravimetrically or colorimetrically. The gravimetric method involves a preliminary separation of the titanium from the hydrogen sulfide group, followed by precipitation of the titanium with Cupferron (nitroso-phenylhydroxylamine) reagent in a sulfuric acid medium. However, the Cupferron reagent not only precipitates titanium but also carries down zirconium, vanadium, iron and the rare earths in part.[34,35] This method results in a high result for titanium; in addition the precipitate formed is very bulky and difficult to ignite.

The colorimetric method for the determination of titanium is the most rapid and most widely used method in the analysis of silicate materials.[36,37,38] It is based on a comparison of the color produced by hydrogen peroxide in a dilute sulfuric acid solution of the material with that obtained in a standard solution of titanic sulfate. Elements that interfere are: (1) iron, nickel, chromium, and the like

---

34. Hillebrand, Lundell, Bright & Hoffman, op.cit., pp. 116, 578.

35. Lundell, G. E. F. and Knowles, H. B., Ind. Eng. Chem. 12, 344, (1920)

36. Shapiro, op.cit.,p. 9.

37. Corey, op.cit., pp. 624-28

38. Shell, op.cit., p. 16.

which interfere because of the color of their solutions; (2) vanadium, molybdenum and, under some conditions chromium, which interfer because they form colored compounds with hydrogen peroxide; and (3) fluorine (even in minute amount) and large amounts of alkali salts or phosphates, all of which bleach the color.[39] Weissler[40] proposed a method for the simultaneous spectrophotometric determination of titanium, vanadium and molybdenum which overcame the interferences due to these elements. Brandt[41] suggests the use of chromotropic acid as the color forming reagent rather than hydrogen peroxide to overcome the interference due to bleaching. However, if care is taken to eliminate the interferences accurate and reproduceable results can be obtained.

The determination of sodium and potassium with the flame photometer has already been discussed and demonstrated to be a very rapid and satisfactory method. Therefore, the following investigation was carried out to develop a procedure for the flame photometric determination of titanium. Since the sensitivity of the Beckman model DU flame photometer was listed as 10 parts per million it appeared suitable for this analysis.

---

39. Hillebrand, Lundell, Bright, Hoffman, op.cit., p. 581

40. Weissler, A., Anal Chem. 17, 695, (1945)

41. Brandt, W. W. and Preiser, A. E., Anal Chem. 25, 567-71, (1953).

In the determination of sodium and potassium the oxyhydrogen flame produces line spectra or atomic spectra when the solutions containing the ions are introduced. Very discrete lines are produced, whose intensities are a function of concentration. Certain molecules such as Ti_xO_y which can exist in the oxyhydrogen flame may be excited to emit band or molecular spectra. The emission of band spectra may be explained in the same general way as the emission of spectral lines from atoms and ions. The molecule can be energized to certain discrete levels or states in an appropriate source; on its return to its original state, it emits radiation in the form of band spectra. The general appearance of the usual band spectrum differs from that of a line spectrum because of a difference in the types of energy levels involved.

A molecular emitter can exist in three types of energy states. Discrete energy levels are associated with (1) the orbital movement of the electron about the molecule (electronic levels), (2) the vibration of each component atom comprising the molecule (vibrational levels), and (3) the rotation of the molecule as a whole (rotational levels). With each electronic level is associated a suite of vibrational levels, and with each vibrational level is associated a suite of rotational levels. Purely electronic transitions involve the largest energy differences and rotational transitions the smallest. These later cause the appearance of fine structure

in a band spectrum.[42] The fine structure is observable only if a large dispersion, such as that obtainable with a large grating spectrograph is used. Whereas fine structure in atomic spectra can be attributed to electron spin, in band spectra it is due to rotation of the molecule. The set of rotational lines corresponding to a particular vibrational transition constitutes a band and every different vibrational transition yields a band of this type. The whole system of vibrational bands for a particular electronic change is called a band group or band system. Each electronic transition that occurs under certain conditions of excitation will yield such a band system, and the series of systems or groups for the different possible electronic changes constitutes the band spectrum of the molecule. Consequently, the emitted radiation is spread over a portion of the spectrum rather than being concentrated in a discrete line. The radiation is centered about the wavelength associated with the electronic transition, with the energy of the bands degraded toward the red or blue portion of the spectrum. Therefore, the bands are not symetrical about any center. Because of the complexity of the perpendicular bands of the Ti_xO_y molecule, it is not possible to resolve the separate rotational lines. Only the band envelope is observed.

---

42. Ahrens, L. H., Spectrochemical Analysis, Addison-Wesley Press Inc.,(1950) p. 145.

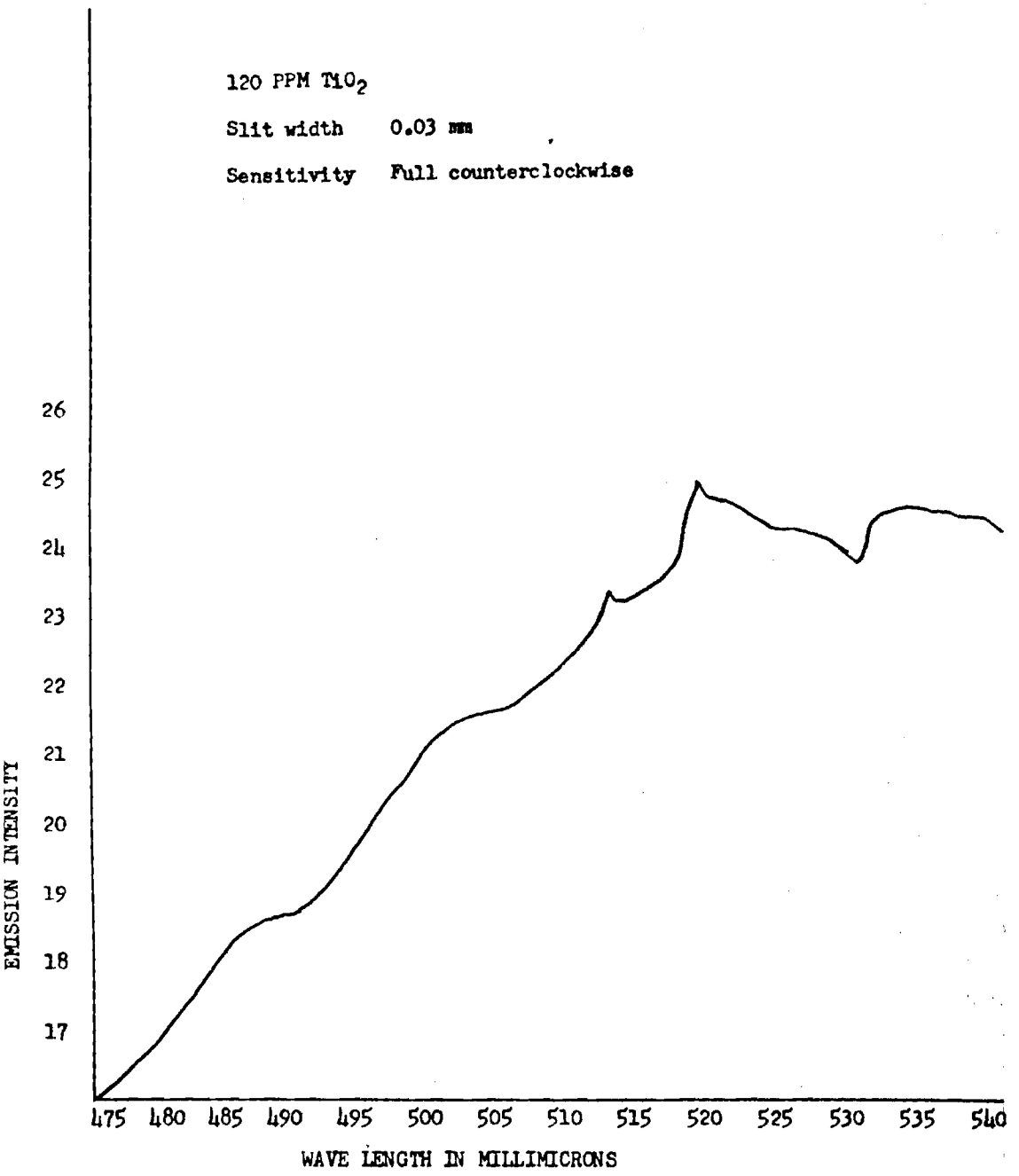


FIGURE 5. EMISSION SPECTRUM OF TITANIUM

Most of the titanium band systems overlap each other. In Figure 5, the flame emission spectrum of titanium is given in the region suitable for flame photometric determination of titanium. The more intense flame emission occurs from the band groupings centered around 540 & 518 m . Since the sharpest emission peak occurred at 518 m all subsequent measurements were made at this wavelength.

The first portion of this investigation involved the study of interferences due to the presence of various cations which are normally present in clay.

Calibration curve. -- A standard stock solution of titanium was prepared by dissolving 1.5197 grams of Bureau of Standards titanium dioxide (Sample #154) in 35 ml of concentrated sulfuric acid containing 15g of ammonium sulfate. The mixture was heated to complete solution, cooled and poured into 450 ml of cold water. After standing 24 hours the solution was filtered and diluted to one liter with 5:95 sulfuric acid. A gravimetric determination of titanium in the stock solution was carried out and the titanium dioxide concentration found to be 1434 ppm.

Standard TiO_2 solutions were prepared from aliquot portions of the stock solutions as shown in Table 7.

Table 7. Standard TiO_2 Solutions

TiO_2 Conc. PPM	Ml of 1434 PPM TiO_2 solution/100 ml
20	1.39
60	4.18
80	5.58
100	6.97
120	8.37
140	9.76
200	13.95

As previously mentioned a Beckman Model DU with Model 9220 flame attachment and photomultiplier unit was used. In the determination of titanium a oxyhydrogen burner was used as an excitation source. The instrument settings used for measuring the titanium flame emission are listed in Table. 8. Unless otherwise specified these settings were used throughout the investigation of titanium.

Table 8. Instrument Settings for the Determination of Titanium

Sensitivity control	Full counterclockwise
Selector switch	0.1
Slit	0.03
Wavelength	518 mμ
Photomultiplier	Full
Hydrogen	5 pounds per square inch
Oxygen	11 pounds per square inch

The emissions of the standard TiO_2 solutions were measured employing the instrument settings listed in Table 8. The emission of the standards and the blank are given in Table 9.

Table 9. Emission of Standard TiO_2 Solutions

TiO_2 Conc. PPM	Emission	Blank H_2O	Corrected Emission
20	7.8	4.7	3.1
60	15.1	4.7	10.4
80	18.2	4.7	13.5
100	21.4	4.7	16.7
120	25.7	4.7	21.0
140	28.7	4.7	24.0
200	39.2	4.7	34.5

A plot of emission vs. concentration of TiO_2 is shown in Figure 6. From this it can be seen that the emission of titanium is a linear function of the concentration. Since there are considerably more variables involved in flame photometric work than in colorimetric work, it was not found advisable to prepare a standard curve as is done in colorimetry for use with unknown samples. A standard curve can be used if care is taken to check several points on the curve with the appropriate standards before an analysis is started. This can be extremely tedious and time consuming whereas, more rapid results can be obtained by bracketing the unknown sample with a standard of higher concentration and one of lower concentration. The latter is the method used in the majority of this work. The concentration of the unknown is calculated by interpolation. It can be assumed that for a small concentration difference the portion of the emission vs. concentration curve used is linear.

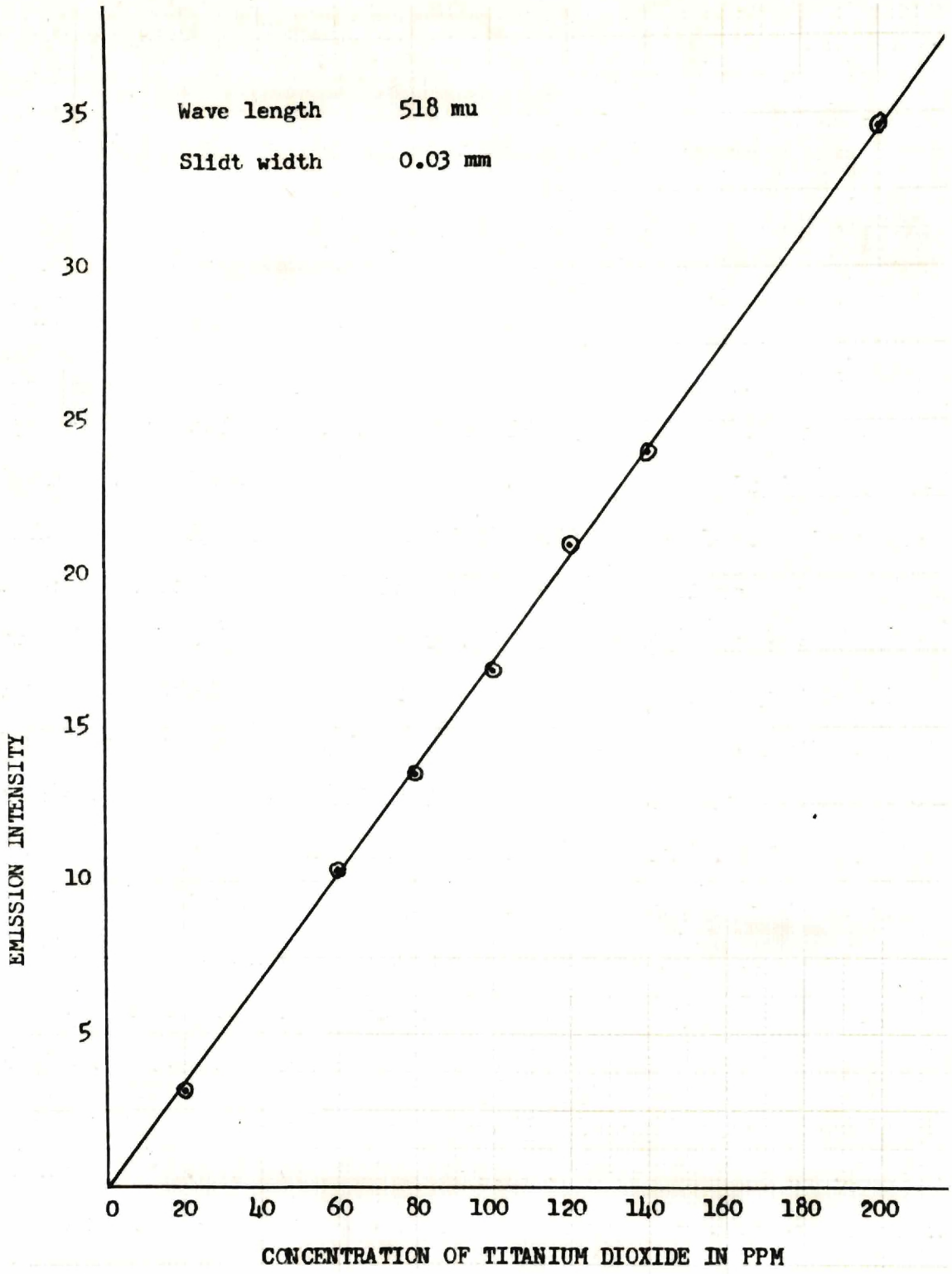


FIGURE 6. STANDARD EMISSION CURVE FOR TITANIUM

A major part of the experimental work in this research was concerned with determining radiation interference, if any, caused by the various cations generally associated with titanium in clay. For each substance tested for interference, a series of solutions was prepared containing several known concentrations of the test substance and generally 20, 60 and 100 ppm of titanium dioxide. Table 10 shows the effect of various cations on the determination of titanium. This data includes those cations which are known to cause serious interference. This interference may be due to strong background radiation such as in the case of potassium. Enhancement from calcium, especially at low titanium concentrations results, unless narrow slit widths are used, since the titanium 518 mμ band is adjacent to the short wavelength side of the prominent calcium 553 mμ band. The interference effects are not attributed entirely to optical effects but, as in the case of aluminum, to absorption of titanium emission energy.[43] This absorption of energy causes a depression in the emission intensity of the titanium. The second series of interference studies included cations which are generally present in clays in low concentrations. The data is given in Table 11. A rather unusual difference in interference is

---

43. Mitchell, R. L., and Robertson, I. M., J. Soc. Chem. Ind., 55, 269--72, (1936)

Table 10. Effect of Cations in the Determination of Titanium by Flame Photometry

Cation Tested	Conc. PPM	TiO_2 Taken Conc. PPM	TiO_2 Found Conc. PPM
Aluminum	550	20	18.6
		60	31.3
		100	48.8
	950	20	28.5
		60	39.2
		100	53.3
	1325	20	33
		60	44.8
		100	58
Calcium	50	20	15.3
		60	23.2
		100	42.6
	100	20	22.6
		60	32.6
		100	39.0
	200	20	32.1
		60	58.4
		100	63.7
	400	20	45.8
		60	67.5
		100	101.6
Potassium	50	20	39.5
		60	77.3
		100	119
	100	20	54.8
		60	96.3
		100	--
	250	20	100
		60	--
		100	--
Sodium	50	20	30.5
		60	78.8
		100	107.9
	100	20	40
		60	76.8
		100	113.7
	250	20	73
		60	107
		100	--

Table 11. Effect of Cations in the Determination of Titanium by Flame Photometry

Cation Tested	Conc. PPM	TiO_2 Taken Conc. PPM	TiO_2 Found Conc. PPM
Iron (Ferrous)	25	100	124
	50	100	145
	75	100	161
	100	100	180
	125	100	198
	150	100	210
Iron (Ferric)	25	100	132
	50	100	153
	75	100	180
	100	100	200
	125	100	219
	150	100	240
Vanadium (V_2O_5)	1.0	100	100
	1.5	100	100
	2.5	100	100
	5.0	100	100
	15.0	100	100
Zirconium (ZrO_2)	2	50	50
		100	100
	10	50	50
		100	100
	15	50	50
		100	100

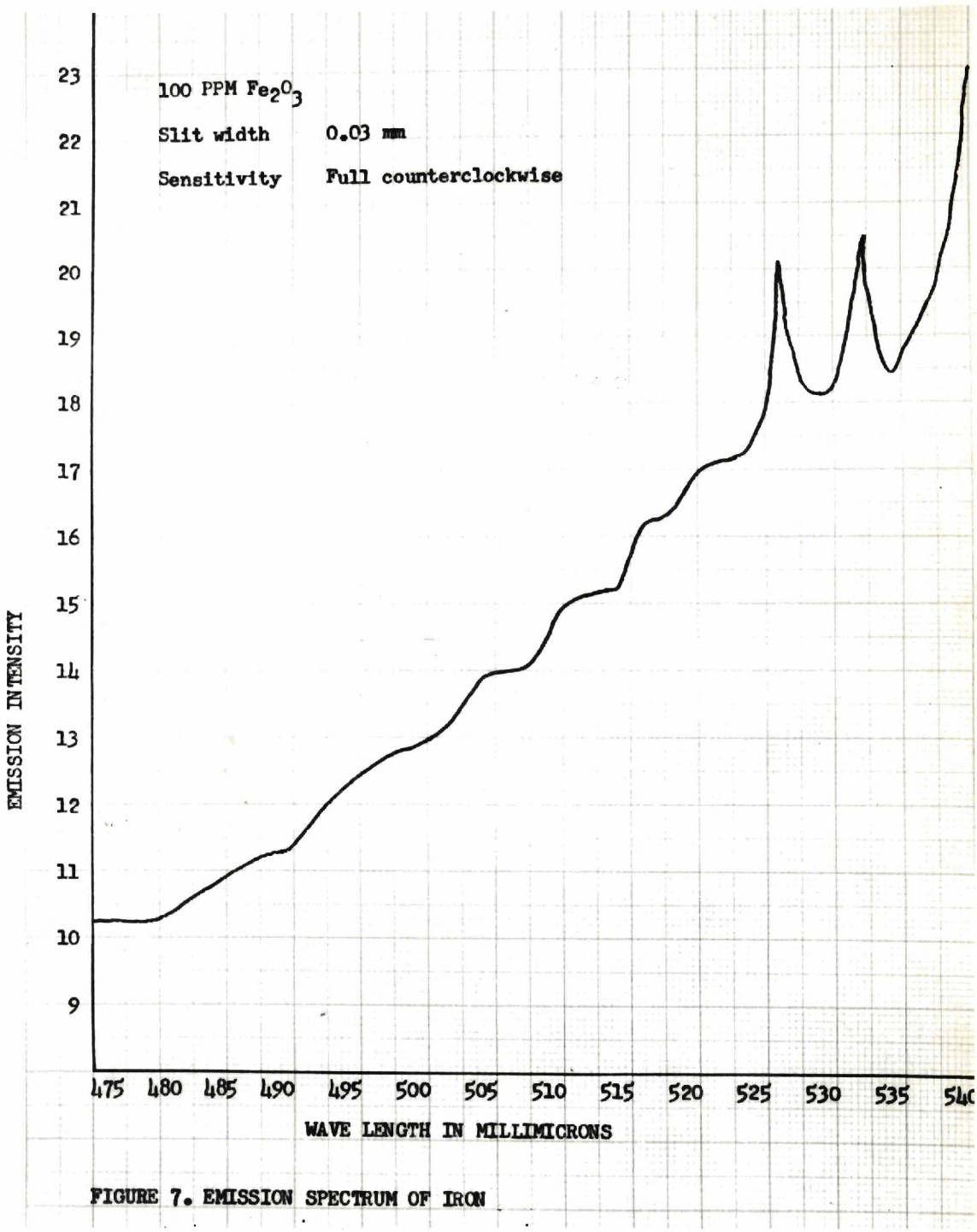


FIGURE 7. EMISSION SPECTRUM OF IRON

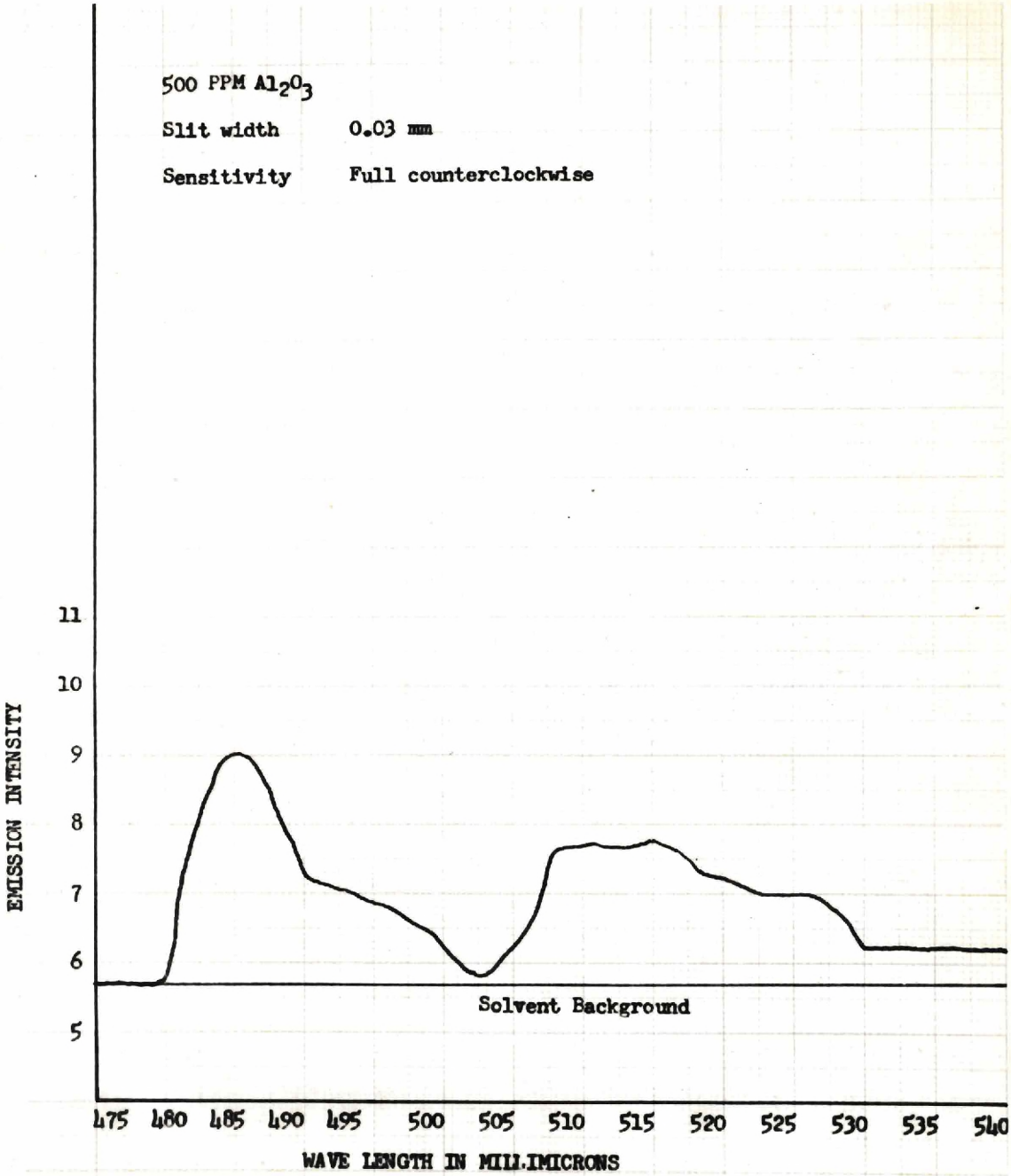


FIGURE 8. EMISSION SPECTRUM OF ALUMINUM

noted between the ferrous and ferric ion. The greater enhancement of the titanium emission by an ion of higher charge of the same element may be due to the difference in excitation potential of the two ions or their activity in the solution. In addition iron has a strong emission at a wavelength of 518 mμ as shown in Figure 7. The background radiation of aluminum and vanadium are given in Figures 8 and 9. The zirconium emission intensity was equal to that of the blank in the region investigated.

The effect of various anions was next determined, chiefly those which were used for the solution of the clay samples or which might be associated with the titanium in the samples. The results are given in Table 12. Chloride ion introduces no error, nitrate ion causes a slight depression when present in high concentration as does sulfate ion. The concentration of these anions that do interfere can be kept at a minimum by careful preparation of the original sample solution.

The interference effects of various cations on the determination of titanium have been shown to be very pronounced. Two alternatives are available in developing a suitable method of analysis. Some type of correction must be made for the interfering ions which are present or they must be removed before the titanium is determined on the flame photometer. The first method, i.e., correcting in some way for the interferring ions would be the most convenient

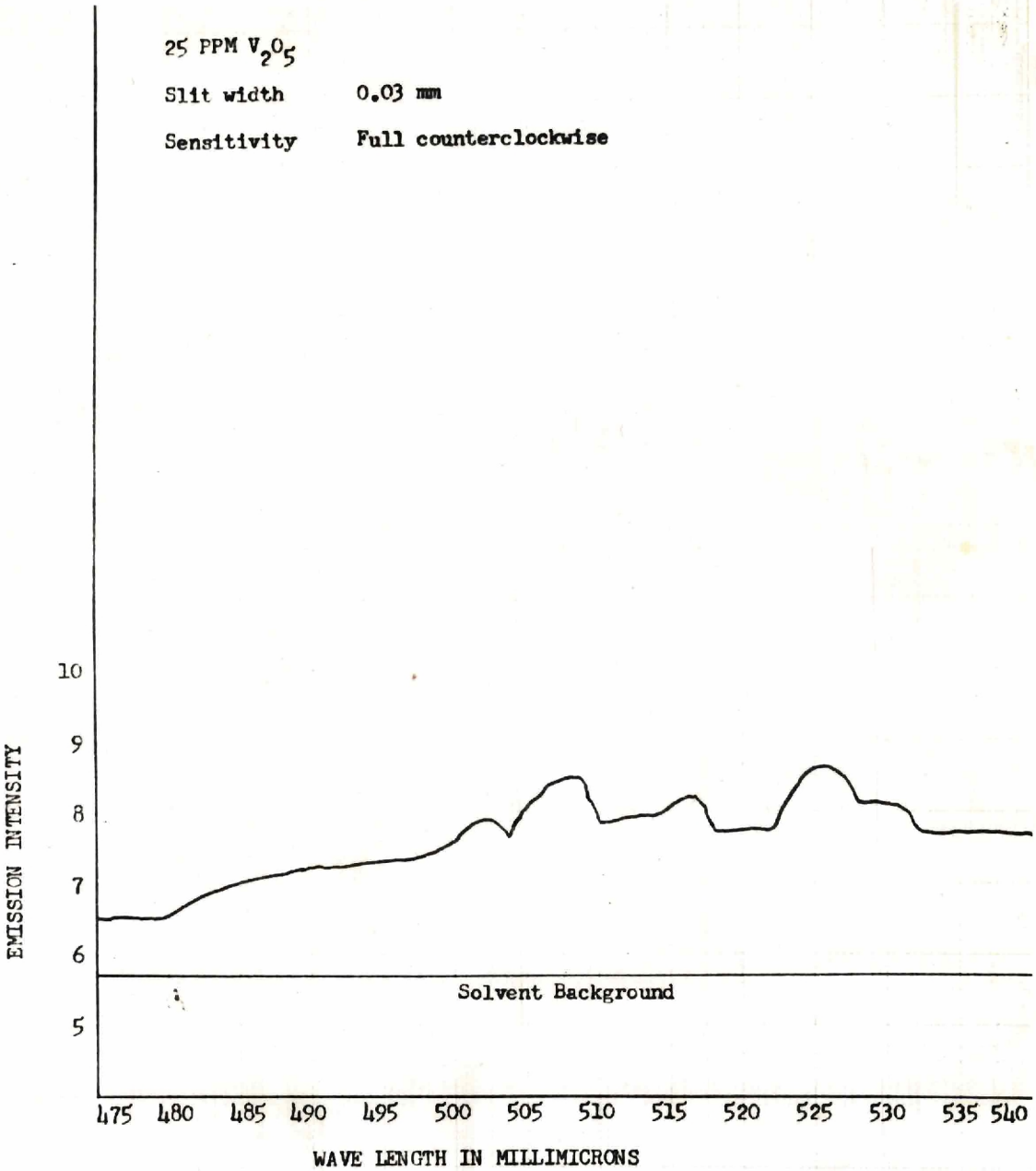


FIGURE 9. EMISSION SPECTRUM OF VANADIUM

Table 12. Effect of Anions on the Determination of Titanium by Flame Photometry

Anion Added	Conc. PPM	TiO_2 Present Conc. PPM	TiO_2 Found Conc. PPM
Nitrate	100	70	70
	500	70	70
	1500	70	70
	3500	70	67.8
Chloride	100	70	70
	500	70	70
	1500	70	70
	3500	70	70
Sulfate	100	70	70
	500	70	70
	1500	70	68.9
	3500	70	65.0

from the standpoint of chemical manipulations.

West,[44] et. al., suggested the use of radiation buffers in flame photometric analysis where samples contained a number of interferring ions. It is based on the idea that if high, consistent concentrations of diverse cations were added to each sample, small concentration variations within the samples themselves would be without effect upon the emission strength of the metal ion to be determined spectrophotometrically.

Radiation buffer solutions were prepared containing high concentrations of aluminum, sodium, potassium and calcium. Synthetic titanium dioxide solutions of 20 and 100 ppm were prepared and various concentrations of the interferring ions added. One milliliter of buffer solution was added to 25 ml of each of the synthetic samples and the emission of each solution and of the buffer solution itself were measured. The overall radiation intensity was considerably higher than normally obtained for the titanium solutions and consequently a much narrower slit width had to be employed. This greatly reduced the sensitivity of the instrument for titanium. In fact the emission of the buffer itself was higher than that of the standard titanium solutions plus the radiation buffer. Due to the high concentration of salts in the sample solution, burner operation was erratic and clogging became a

---

44. West, P. W., Folse, P., and Montgomery, D., Anal. Chem., 22, 667, (1950)

major problem. It appeared that although the overall effects of the interferring ions had been reduced the method was found to be seriously lacking in accuracy and reproduceability. Therefore, this method was eliminated as a possible solution to the problem.

The overlapping band systems of titanium presented a problem not often encountered in flame analyses, i. e., how to choose a general background reference wavelength. Usually one refers to the general background reading in the vicinity of the band head or emission line in order to determine the correction to be applied to the observed emission at the wavelength of the band head or emission line. Because the band systems of titanium overlap in the useful region, this procedure is not possible. Dean[45] suggests that the minimum intensity in the troughs will serve the same purpose as a normal background reading. Dean's work involved the flame photometric determination of boron whose emission spectrum includes much sharper band peaks than does the titanium spectrum. Referring to Figure 5, it is noted that only one sharp peak is observed and that lies at 518 mμ. The minimum intensity in the nearest trough is at 502 mμ. In this method the intensity of emission of titanium standards is measured at the band peak, which is 518 mμ, and then at the trough,

---

45. Dean, op.cit., p. 42.

which is around 502 mμ. The difference between these two values is a measure of the titanium concentration in the solution. Any interferring ions present should have the same effect on the emission of titanium at 518 mμ as they do at the lower wavelength. This is true providing a strong band or line is not emitted by the test cation which coincides with or overlaps the titanium band head or adjacent rough minimum.[46] Since a strong band is emitted by iron around 518 m it had to be removed from the solution. The iron was removed by precipitation with hydrogen sulfide in the presence of tartaric acid. The solutions were acidified with concentrated sulfuric acid and boiled to remove hydrogen sulfide. Table 13 lists the results of this method.

Table 13. Results of Titanium Analysis Using The Method of Dean[13]

Emission in Scale Divisions					
Wavelength 518 mμ	Wavelength 502 mμ	Difference 518mμ-502mμ	TiO_2 Present	TiO_2 Found	Sample
18.3	16.3	2.1	80ppm	-	-
25.8	22.9	2.9	120ppm	-	-
39.8	34.3	5.5	200ppm	-	-
15.8	14.2	1.6	2.38%	2.38%	97x
16.0	14.5	1.5	2.38%	2.30%	97y
17.0	16.0	1.0	1.43%	1.47%	98x
16.8	15.8	1.0	1.43%	1.42%	98y
15.3	14.1	1.2	100ppm	99ppm	I

46. Dean, op.cit., p. 43.

The results reported in Table 13 are in close agreement with the amounts of TiO_2 actually present in the sample. However, on examination of the emission intensities very little difference in the intensities is noted on changing wavelength. This is due to the fact that the emission band peak is not sharp but gradually decreases to a wavelength of about 400 mμ. There is only a slight difference in emission intensity between the peak at 518 mμ and the trough at 502 mμ. Although satisfactory results were obtained, the method would not be suitable for routine analysis. An error of 0.1 units in reading the emission intensity would result in an error of about five parts per million. It is difficult to reproduce readings on the Beckman instrument to within 0.1 units so this method was also discarded.

The alternate method for titanium analysis by flame photometry as previously mentioned must involve some chemical separation. From the date in Tables 10 and 11 it is observed that the largest interferences are due to the alkali metals, calcium and iron. The removal of the former can be accomplished by ppt. with ammonium hydroxide and the latter by precipitation with hydrogen sulfide in the presence of tartaric acid. The sample solution after these separation procedures would contain titanium, aluminum, vanadium and zirconium. Since it was demonstrated that vanadium and zirconium had no effect on the emission of titanium the only interference remaining would be that due to aluminum. To overcome

this difficulty the possibility of using the internal standard method of flame photometric analysis outlined by Chow and Thompson[47,48] was investigated.

Synthetic TiO_2 sample solutions were prepared containing various concentrations of interferring ions as listed in Table 14.

Table 14. Synthetic TiO_2 Sample Solutions

Soln.	TiO_2 Conc. PPM	Sodium Conc. PPM	Potassium Conc. PPM	Calcium Conc. PPM	Aluminum Conc. PPM	Fe_2O_3 Conc. PPM	V_2O_5 Conc PPM	ZrO_2 Conc PPM
I	100	50	50	50	500	100	1	5
II	100	250	250	250	1000	300	3	15
III	60	150	150	150	500	150	1	10

Four 5 ml portions of each of solutions I, II and III listed in Table 14 were taken. To one portion, 5 ml of distilled water was added while to the other three portions there was introduced 5 ml of standard titanium dioxide solution, each portion receiving a standard of different concentration of titanium. The emission intensity of these twelve portions was determined with the Beckman flame photometer. The emission intensity was plotted against the titanium dioxide concentration of the standards added. If there are no interferences besides background radiation a straight line should

47. Chow, T. J., and Thompson, T. G., Anal. Chem. 27,18,(1955)
48. Ibid, p. 910

be obtained. The combined net intensity of the light was that emitted by titanium in the standard, plus the titanium in the unknown. If there were any interferring substances existing in the solution they affected equally the emission of the light resulting from that of the standard and the unknown. The line intersecting the ordinate indicated the emission intensity of titanium in the unknown. If the graph of emission intensity vs. concentration of titanium is a straight line ($Y = a + bx$) the unknown titanium concentration x is given by the ratio of Y (the emission intensity of the unknown) to the slope of the line, when $a = 0$. The emission intensity of the unknown must be double because it was diluted with an equal volume of water. With this value the concentration of titanium could then be read off the graph. However, the plot of emission intensities vs. concentration for samples I, II and III did not yield a straight line. The addition of increasing concentrations of standard TiO_2 solutions had little effect on the emission. The sample solutions themselves had a high emission and the addition of TiO_2 solution caused only a slight increase in emission. No calculation of titanium concentrations could be made from the data obtained.

The next step was to undertake some separation procedure to eliminate the ions which caused the most serious interference. This procedure would of necessity involve the removal of the alkali metals, alkaline earths and iron. The

following procedure was adopted: A 50 ml aliquot of the original clay sample solution was transferred to a 250 ml beaker and diluted to about 150 ml. Two grams of ammonium chloride were added and the solution heated to boiling. After the addition of three drops of methyl red the solution was neutralized with 1:1 ammonium hydroxide, heated to boiling and filtered through Swedish #1F grade paper. The precipitate was washed with warm two percent ammonium nitrate solution, and then dissolved into a 250 ml beaker with hot 1:1 hydrochloric acid. An amount of tartaric acid was added which was about equal to the weight of metallic oxides which would be obtained on ignition of the ammonium hydroxide precipitate. The solution was saturated with hydrogen sulfide to reduce the iron, neutralized with 1:1 ammonium hydroxide and again saturated with hydrogen sulfide. The solution was digested at the boiling temperature to agglomerate the precipitated ferrous sulfide and then filtered through number 8 grade filter paper. The precipitate was washed with one percent ammonium tartrate. Five ml. of concentrated sulfuric acid was added to the filtrate and the solution boiled to expel hydrogen sulfide. After cooling the solution was transferred to a 50 ml volumetric flask and diluted to volume. The sample was then ready for flame photometric determination of titanium by the internal standard method. The solution undoubtably contained traces of the alkali metals, alkaline earths and iron due to incomplete

separations. However, it was believed that this method would overcome these difficulties. The results of analysis of the synthetic samples by the internal standard method are given in Table 15.

Table 15. Results of TiO_2 Determination by Internal Standard Method

Solution	TiO_2 Present Conc. PPM	TiO_2 Found Conc. PPM
Ia	100	100
Ib	100	190
Ic	100	157
Id	100	150
IIa	100	220
IIb	100	200
IIIa	60	125
IIIb	60	80

The results obtained by the internal standard method were extremely erratic and in most cases considerably higher than the actual titanium concentration. In most cases a plot of emission vs. titanium concentration did not yield a straight line. The failure of this method is probably due to incomplete separation of the titanium from the alkali metals and especially iron. The internal standard method was thus eliminated as a possible method for titanium analysis.

The last approach used was one involving chemical separation and preparation of standards similar in composition to the sample. This is a practice commonly employed in

flame photometric analysis.[49,50,51] The following is the procedure finally adopted for the determination of titanium in clay employing the flame photometer.

The clay sample is dissolved according to the procedure employing an H_2SO_4-HF mixture as in Chapter II. A 50 ml aliquot of this sample solution is transferred to a 250 ml beaker, diluted to 150 ml and two grams of ammonium chloride added. The solution is heated to boiling, three drops of methyl red are added and the solution neutralized with 1:1 ammonium hydroxide. The solution is boiled for one minute and then filtered through Swedish #1F grade filter paper. The precipitate is washed with hot 2% ammonium nitrate and then dissolved into a 250 ml beaker with hot 1:1 hydrochloric acid. The precipitation is repeated to remove the last traces of alkali metals and alkaline earths. After redissolving the precipitate with hot 1:1 hydrochloric acid the solution is transferred to a 100 ml volumetric flask and diluted to volume. This solution should be essentially free from the alkaline earths, alkali metals, magnesium and any other constituents that may be present in the clay and are not precipitated by ammonium hydroxide. The solution is

---

49. Bauserman, H. M., and Cerney, R. R. Jr., Anal. Chem., 25, 1821, (1953)

50. Williams, J. P., Adams, P. B., J. Amer. Cer. Soc., 37, 306, (1954)

51. Kuemmel, D. F. and Karl, H. L., Anal. Chem., 26, 386, (1954)

now ready for the analysis of titanium on the flame photometer.

The sample solution to be analyzed for titanium contains not only aluminum and iron but also vanadium and zirconium. The interference studies showed that vanadium and zirconium did not interfere with titanium emission so there remains only the problem of correcting, for the aluminum and iron interference. This interference can be overcome by preparing standards containing aluminum and iron of concentrations approximating that found in the sample. The iron can be determined on the flame photometer using a portion of the solution employed for the flame photometric determination of titanium.[52] Aluminum may be determined colorimetrically[53] or gravimetrically as the 8-hydroxyquinolate.[54]

The standard titanium solutions to be used for the determination of titanium are prepared by transferring the required amount of titanium stock solution to 50 ml volumetric flasks and then adding the approximate concentrations of aluminum and iron that were present in the samples. Standards of 50 and 88 ppm titanium were prepared in this manner. Only two standards were prepared since the concentration of TiO_2

---

52. Dean, J. A., and Burger, J. C. Jr., Anal Chem., 27, 1052, (1955)

53. Corey, op.cit. p. 625

54. Hillebrand, Lundell, Bright, Hoffman, op.cit. p. 507

in the samples was known to be within this range. For unknown samples it is advisable to run a rough determination to aid in preparing standards of the proper range. The emission of each set of standards was measured followed by the sample whose aluminum and iron concentration corresponded to that set of standards. This procedure was repeated for each sample and the average of three readings recorded. Since the flame intensity fluctuates considerably from day to day, no standard curve was prepared. The concentration of titanium in the unknown was obtained by interpolation of the emission values obtained for the various standards. Table 16 gives a summary of results obtained by this method for titanium analysis.

The results in all cases are slightly high which probably is attributeable to the presence of traces of alkalies which were not completely removed in the separation procedures. The emission values and a sample calculation for the titanium analyses are contained in Table 23. (appendix).

Table 16. Results of Flame Photometric Determination of Titanium by Synthetic Standard Method

Sample	TiO_2 Taken Conc. PPM	TiO_2 Found Conc. PPM	Error
Ia	100	102.5	2.5 ppm
Ib	100	103.8	3.8
IIa	100	106.2	6.2
IIb	100	107.0	7.0
IIIa	60	64.3	4.3
IIIb	60	61.0	1.0
	TiO_2 Present Conc. percent	TiO_2 Found Conc. percent	Error
97v.	2.38%	2.40%	.02%
97z	2.38	2.41	.03
98v	1.43	1.45	.03
98z	1.43	1.47	.04
T-1v[3]	1.26	1.30	.04
T-2v	1.42	1.45	.03
T-2z	1.42	1.47	.05

Composition of Samples I, II and III is given in Table 14. Samples 97 and 98 are Bureau of Standard clays. Samples T-1 and T-2 are Kaolinite from Georgia.

SUMMARY

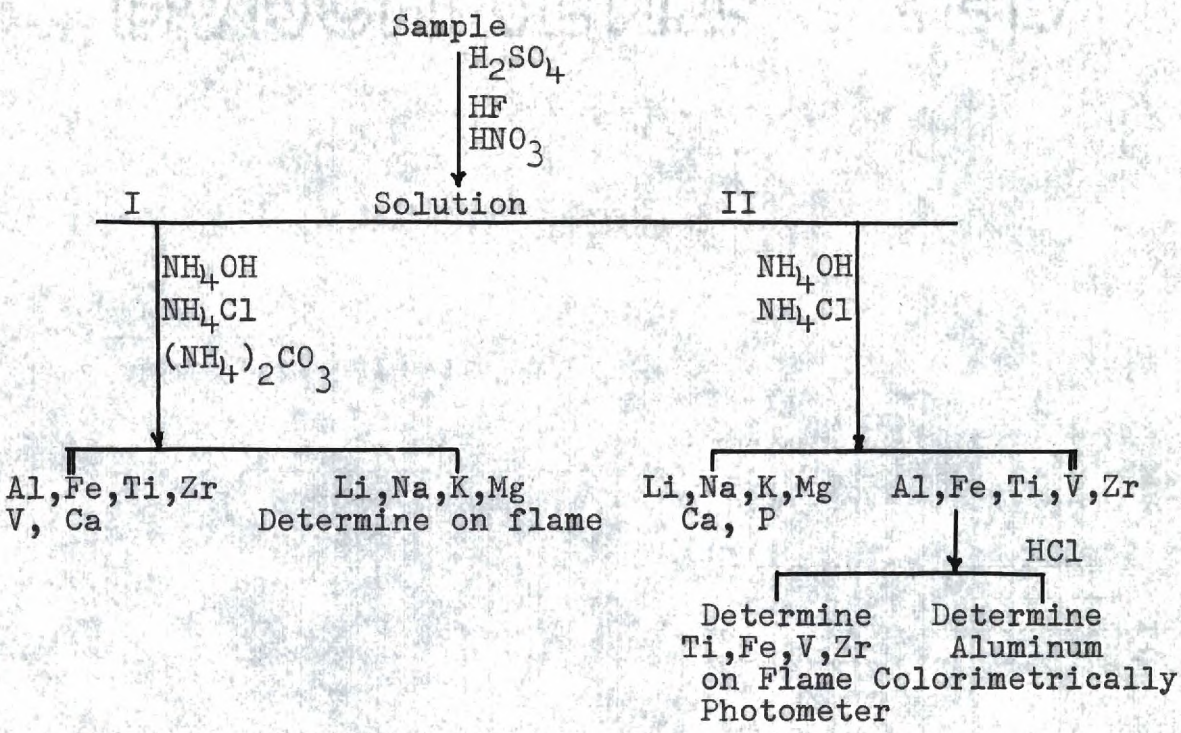
A flame spectrophotometric method for the determination of sodium, potassium and titanium in clay has been presented. The clay sample is brought into solution by digestion with a mixture of 1:1 H_2SO_4, concentrated HF and sufficient concentrated HNO_3 to destroy all the organic matter which may be present. Aliquot portions of the sample solution are taken for subsequent analysis. The flame photometric analysis of sodium and potassium are performed on the same sample aliquot while a second aliquot is necessary for the determination of titanium.

A complete study of interferences due to foreign ions, which are normally present in clays, was carried out. Since the interferences due to metals which precipitate with NH_4OH, such as aluminum and iron, are large; these metals must be removed before the flame analysis of sodium and potassium can be carried out. This is accomplished by adding NH_4OH to the volumetric flask containing the sample aliquot, then diluting to volume. The solution is filtered or contrifuged prior to flame analysis. The results are comparable to those obtained by lengthy conventional methods.

The determination of titanium by flame spectrophotometry is affected not only by iron and aluminum, but also very markedly by the alkali metals and alkaline earths. These interferences necessitate a chemical separation before analysis.

The titanium is separated from the alkalies, magnesium and phosphorous by precipitation with NH_4OH in the presence of NH_4Cl. The precipitate is then dissolved in 1:1 HCl. A double precipitation and thorough washing is necessary for complete separation. Since aluminum and iron also interfere with titanium analysis, a correction must be made for their presence. This is done by preparing standard TiO_2 solutions containing approximately the same concentrations of aluminum and iron as the samples to be analyzed. Titanium concentrations as low as ten parts per million can be determined by this method. Results are slightly higher than the colorimetric results probably due to incomplete removal of the alkalies.

The solution obtained by dissolving the ammonium hydroxide precipitate in HCl not only contains aluminum, iron and titanium, but also vanadium and zirconium. By selecting the proper wavelength the vanadium and zirconium can also be determined by flame photometry. Magnesium can be determined in the solution used for the sodium and potassium analysis. These additional determinations were not thoroughly investigated since the additional time necessary was not available. Preliminary work, however, indicated that satisfactory results could be obtained. The following outline gives an overall picture of the application of flame spectrophotometry to the analysis of clay.



This outline emphasizes the extent to which the flame photometer can be utilized in the determination of substances which are present in only small amounts in clays.

APPENDIX

Table 17. Emission Intensities of Standard Sodium Chloride Solutions.

Sodium Conc. PPM	Emission	Blank H_2O-$(NH_4)_2SO_4$	Corrected Emission
5	7.1	.2	6.9
10	12.9		12.7
25	24.0		23.8
50	37.1		36.9
100	52.1		51.9

Table 18. Emission Intensities of Standard Potassium Chloride Solutions

Potassium	Emission	Blank H_2O-$(NH_4)_2SO_4$	Corrected Emission
5	5.2	0	5.2
10	9.7		9.7
25	21.5		21.5
50	37.1		37.1
100	57.9		57.9

Table 19. The Effect of Potassium on the Determination of Sodium by Flame Spectrophotometry.

Solution	Potassium Conc. PPM	Corrected Emission	Difference	Correction Subtract from Na Conc. PPM
50ppm Na	0	37.0		
I	10	37.0	0	0
II	25	37.0	0	0
III	50	37.1	.1	0.2
IV	60	37.2	.2	0.5
V	75	37.4	.4	0.9
VI	90	37.5	.6	1.4
VII	100	37.7	.7	1.7
VIII	110	37.8	.8	1.9
IX	125	37.9	.9	2.1

All solutions contained 50 ppm sodium and 3 g of ammonium sulfate.

Table 20. Emission Data for the Determination of Sodium in a Series of Samples.

Standards	Emission Intensity	Blank Correction	Corrected Emission	Sodium Conc. PPM	Na_2O Percent
5	10.0	.2	9.8	5	
10	17.2		17.0	10	
25	30.8		30.8	25	
50	44.1		43.9	50	
100	60.1		59.9	100	
Samples					
T-1	3.2	2.0	1.2	1.23	.03
T-2	10.0		8.0	8.2	.20
T-3	6.2		4.0	4.0	.10
T-5	43.3		41.3	90.4	2.15
#97	4.9		2.9	2.96	.07
#98	11.8		9.8	10.0	.28

SAMPLE CALCULATION

$$\text{Conc. PPM of Sodium} = 2 \times \left[A + \left(\frac{Y - X}{X_1 - X} \right) \times \Delta C \right]$$

Y = Emission of sample.
X = Emission of standard whose concentration is slightly less than that of the sample.
X_1 = Emission of standard whose concentration is slightly greater than that of the sample.
A = PPM of sodium in standard whose concentration is slightly lower than that of the sample.
ΔC = Difference in sodium concentration between the higher standard and the lower standard in PPM.

For example using the data given for sample T-5 in Table .

$$\text{Conc. PPM of Sodium} = 2 \times \left[25 + \left(\frac{41.3 - 30.8}{44.1 - 30.8} \right) \times 25 \right]$$

$$= 90.4 \text{ PPM}$$

$$\% \, Na_2O = \frac{\text{Conc of Na in PPM} \times Na_2O}{100 \times \text{Sample Wgt.} \times 2 \text{ Na}}$$

$$= \frac{90.4 \times 62}{100 \times .5061 \times 46}$$

$$= 2.15\% \; Na_2O$$

Note: The concentration of sodium in parts per million must be doubled since a 25 ml aliquot of the sample solution was taken and diluted to 50 ml.

Table 21. Emission Data For the Determination of Potassium in a Series of Samples.

Standards	Emission Intensity	Blank Correction	Corrected Emission	Potassium Conc. PPM	K_2O Percent
5	5.3	.2	5.1	5	
10	10.1		9.9	10	
25	22.2		22.0	25	
50	37.7		37.5	50	
100	59.6		59.4	100	
Samples					
T-1	3.1	.2	2.9	5.8	.15
T-2	3.7		3.5	7.0	.18
T-3	1.0		0.8	1.6	.04
T-5	8.2		8.0	16.0	.42
#97	10.6		10.4	20.8	.55
#98	39.5		39.3	10.8	3.40

Table 22. Results of Flame Photometric Determination of Sodium and Potassium.

Sample	Na_2O Percent	K_2O Percent	Sample	Na_2O Percent	K_2O Percent	Sample	Na_2O Percent	K_2O Percent
	.07	.51		10.72	.43		.13	.02
	.05	.52	B.S. #99	10.68	.42		.10	.04
	.05	.51	Feldspar	10.73	.42		.11	.05
	.05	.59		10.70	.41	A.P.I T-3	.12	.05
	.05	.59				Clay	.11	.05
	.05	.54					.12	.05
B.S. #97	.05	.54		.06	.30		.14	.06
Clay	.04	.54	B.S.#102	.06	.30		.13	.04
	.04	.54	Silica	.05	.32		.10	.05
	.07	.55	Brick	.06	.31			
	.07	.57						
	.06	.53					2.06	.46
				.03	.15		2.14	.41
	.27	3.25	A.P.I T-1	.03	.15	A.P.I T-5	1.98	.44
	.24	3.36	Clay	.04	-	Clay	2.17	.41
	.28	3.59		.05	.18		2.18	-
	.28	3.56		.04	.19		2.15	.42
	.30	3.62					2.20	.45
B.S. #98	.24	3.25		.20	.18			
Clay	.25	3.38		.19	.17			
	.29	3.27		.20	.19			
	.27	3.24	A.P.I T-2	.20	.18			
	.28	3.40	Clay	.20	.18			
	.27	3.32		.20	.18			
				.21	.18			
				.19	.14			

Table 23. Emission Values For Standards and Samples In The Flame Photometric Determination of Titanium.

Solution	Emission	Blank	Corrected Emission	TiO_2 Found Conc. PPM	TiO_2 Found Conc. %	TiO_2 Present
50a	15.3	5.0	10.3			50 ppm
80a	17.3		12.3			80 "
97v	16.0		11.0	121.4	2.40	2.38 %
97z	16.0		11.0	121.4	2.41	2.38 %
50b	16.0	5.0	11.0			50 ppm
80b	18.1		13.1			80 "
98v	13.0		8.0	73.0	1.46	1.43 %
98z	13.1		8.1	73.6	1.47	1.43 %
50c	14.3	5.0	9.3			50 ppm
80c	16.2		11.2			80 "
T-1v	11.1		6.1	66	1.30	1.26 %
50d	14.2	5.0	9.2			50 ppm
80d	16.0		11.0			80 "
T-2v	11.7		6.7	72.6	1.45	1.42 %
T-2z	11.9		6.9	74.4	1.47	1.42 %

$$\% TiO_2 = \frac{\text{Conc. PPM}}{100 \times \text{wgt of sample}} \qquad \text{Conc. PPM } TiO_2 \text{(Sample 97v)} = 2 \times \left[50 + \frac{11.0 - 10.3(30)}{12.3 - 10.3} \right]$$

$$T\ TiO_2 = \frac{121.4}{100 \times 0.5056} \qquad = 121.4 \text{ ppm}$$

$$\% TiO_2 = 2.40$$

Note: The Concentration in ppm must be doubled since a 25 ml aliquot of the sample solution was taken and diluted to 50 ml.

BIBLIOGRAPHY

1. Ahrens, L. H., Spectrochemical Analysis, Addison-Wesley Press Inc., (1950) p. 145.

2. Barry, J. W., Chappell, D. G. and Barnes, R. B., Improved Method of Flame Photometry, Industrial and Engineering Chemistry, Analytical Edition, 18, pp. 19-24 (1946).

3. Bauserman, H. M., and Cerney, R. R. Jr., Flame Spectrophotometric Determination of Sodium and Potassium, Analytical Chemistry 25, p. 1821 (1953).

4. Brannock, W. W., and Berthold, S. M., The Determination of Sodium and Potassium in Silicate Rocks by Flame Photometer, Geological Survey Bulletin, 992 (1949) p. 3.

5. Brandt, W. W., and Preiser, A. E., Spectrophotometric Investigation of Reaction of Titanium with Chromotropic Acid, Analytical Chemistry, 25, p. 567 (1953).

6. Chow, T. J., and Thompson, T. G., Flame Photometric Determination of Strontium in Sea Water, Analytical Chemistry, 27, p. 18 (1955).

7. Corey, R. B., and Jackson, M. L., Silicate Analysis by a Rapid Semimicrochemical System, Analytical Chemistry, 25, p. 624, (1953).

8. Dean, J. A., and Burger, J. C., Jr., Flame Spectrophotometric Determination of Iron in Siliceous Materials, Analytical Chemistry, 27, p. 1055, (1955).

9. Diamond, J. J., and Bean, L., Use of the Beckman and Perkin-Elmer Flame Photometers for the Determination of Alkalies in Portland Cement, American Society for Testing Materials, Special Technical Publication No. 116, p. 28 (1951).

10. Diamond, J. J., and Bean, L., Improvements in Flame Photometric Determination of Sodium in Portland Cement, Analytical Chemistry, 25, p. 1825, (1953).

11. Eggertsen, F. T., Garrard, W., and Lykken, L., Control of Interferences Caused by Acids and Salts in the Flame Photometric Determination of Sodium and Potassium, American Society for Testing Materials, Special Technical Publication No. 116, p. 58, (1951).

12. Ford, C. L., Determination of Sodium, and Potassium Oxides in Portland Cement by Flame Photometry, Analytical Chemistry, 26, p. 1578 (1954)

13. Gilbert, P. T., Howes, R. C., and Beckman, A. O., Beckman Flame Spectrophotometer, Analytical Chemistry, 22, p. 772 (1950)

14. Gilliland, J. L., Applications of Flame Photometry for the Analysis of Alkalies in Silicates, Waters and Metals, American Society for Testing Materials, Special Technical Publication No. 116, 33, (1951).

15. Glasstone, S. Textbook of Physical Chemistry, D. Van Nostrand Co., Inc., pp. 1132, 1133, (1940).

16. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., Applied Inorganic Analysis, Second Ed., John Wiley and Sons, Inc., (1953).

17. Kinsvark, O. N., Wittwer, S. W., and Sell, H. M., Flame Photometric Determination of Calcium, Strontium and Barium in a Mixture, Analytical Chemistry, 25, p. 320, (1953).

18. Knight, S. B., Mathis, W. C., and Graham, J. R., Mineral Analysis With the Flame Photometer, Analytical Chemistry, 23, p. 1704 (1951).

19. Kuemmel, D. F., and Karl, H. L., Flame Photometric Determination of Alkali and Alkaline Earth Elements in Cast Iron, Analytical Chemistry, 26, p. 386 (1954).

20. Lundegardh, H., Die Quantitative Spectroanalyse der Elemente, pt. 1, Jena, Gustave Fisher, (1929).

21. Lundell, G. E. F., and Knowles, H. B., The Use of Cupferron in Quantitative Analysis, Industrial and Engineering Chemistry, 12, p. 344, (1920).

22. McCoy, W. J., and Christiansen, G. G., The Determination of Lithium Oxide in Portland Cement by Flame Photometer, American Society for Testing Materials, Special Technical Publication No. 116, p. 44 (1951).

23. Mitchell, R. L., and Robertson, I. M., The Effect of Aluminum on the Flame Spectra of the Alkaline Earths, Journal of the Society of Chemical Industry, 55, p. 269 (1936).

24. Mosher, R. E., Bird, E. J., and Boyle, A. J., Flame Photometric Determination of Calcium in Brucite and Magnesite, Analytical Chemistry, 22, (1950).

25. Porter, P., and Wyld, G., Elimination of Interferences in Flame Photometry, Analytical Chemistry, 27, p. 733, (1955).

26. Scott, W. W., Standard Methods of Chemical Analysis, Fifth Ed., Vol. I, D. Van Nostrand and Co., Inc. (1939).

27. Shapiro, L. and Brannock, W. W., Rapid Analysis of Silicate Rocks, Geological Survey Circular, 165, (1952).

28. Shell, H. R., Chemical Analysis of Clay, Bureau of Mines Report of Investigations, 4420, (1949).

29. Weissler, A., Simultaneous Spectrophotometric Determination of Titanium, Vanadium and Molybedenum, Analytical Chemistry, 17, 695 (1945).

30. West, P. W., Folse, P., and Montgomery, D., Application of Flame Spectrophotometry to Water Analysis, Analytical Chemistry, 22, 667, (1950).

31. Williams, J. P., Adams, P. B., Flame Spectrophotometric Analysis of Glasses and Ores, Journal of the American Ceramics Society, 37, 306, (1954).